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Electronic Supplementary Information

Reversible OH-Bond Activation and Amphoterism by Metal-Ligand Cooperativity of the Calix[4]pyrrolato Aluminate

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S-1. Materials and methods

All used reagents and solvents were purchased from commercial sources. Unless otherwise noted, all manipulations were carried out under a dry nitrogen or argon atmosphere. Solvents were degassed prior to use with four freeze-pump-thaw cycles and were stored in sealed Schlenk ampulla over activated molecular sieve (3 or 4 Å, respectively) under a dry argon atmosphere. Liquid reactants were degassed for at least 10 min with a constant stream of dry argon through the fluid phase and were dried by storage over activated molecular sieve (3 or 4 Å, respectively). Solid reagents were dried and purified if necessary either by the application of vacuum and elevated temperature, or by sublimation under reduced pressure at elevated temperature.

All reactions on preparative scale were carried out in flame-dried standard laboratory glassware under a dry argon atmosphere using Schlenk line techniques and were permanently magnetically stirred. Syringes, magnetic stirring bars, and needles were dried and/or flushed with argon prior to use. Reaction on the NMR sample scale were done in dry J. Young NMR tubes.

Compounds sensitive to ambient conditions were handled and stored in a Sylatech glove box filled with dry nitrogen gas. Removal of solvents *in vacuo* was performed using a Heidolph VV2000 rotary evaporator or a Schlenk line.

Literature-known compounds were synthesized following published procedures, which are cited (see below). Analytical data of known compounds were compared to data of the respective reference and were found to be consistent in all cases. Novel compounds were characterized to the reported structures to the best of our knowledge.

Nuclear magnetic resonance (NMR) spectra were collected with a Bruker BZH 200/52, a Bruker DPX 200, a Bruker Avance II 400, or a Bruker Avance III 600 spectrometer at 298 K unless otherwise noted. Measurements with the Bruker Avance spectrometers were carried out by the NMR facility of the Institute of Inorganic Chemistry of the University of Heidelberg.

Chemical shifts δ are given in parts per million (ppm) relative to the tetramethylsilane resonance. Deuterated dichloromethane, tetrachloroethane (in one case), and tetrahydrofuran were used as solvent in all cases, and the signal of $CHDCl_2$ and THF-d_7 was used for calibration of the spectra (CD_2Cl_2: ^{1}H: 5.32 ppm, ^{13}C: 53.84 ppm, THF-d_8: ^{1}H: 3.58 ppm, ^{13}C: 67.21 ppm). ^{1}H NMR data is reported as follows: chemical shift δ [ppm], multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, spet = septet, m = multiplet), scalar spin-spin coupling constant [Hz] as $^XJ_{AB}$ (X = number of chemical bonds between coupled nuclei; A, B = coupled nuclei), integration value, signal assignment. $^{13}C\{^1H\}$ NMR data is reported as follows: chemical shift δ [ppm], multiplicity (only for $^XJ_{CP}$, d = doublet), type of carbon atom (CH_3, CH_2, CH, C_q), signal assignment.

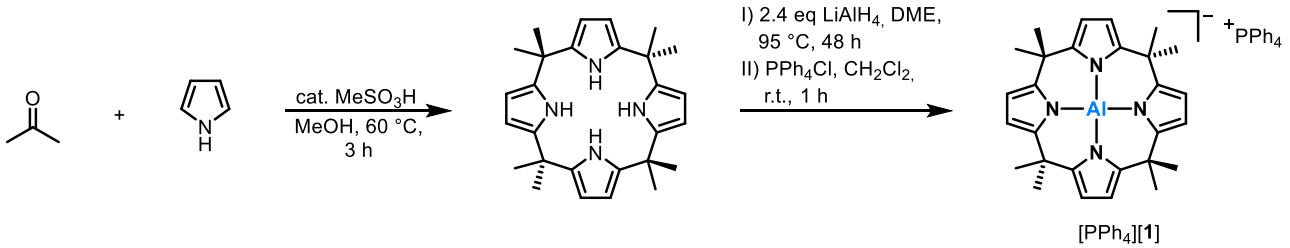
The protons of the aromatic pyrrole rings of the calix[4]pyrrolato ligand are denoted "β-H", the respective carbon atoms "β-C". The quaternary carbon atoms of the aromatic pyrrole rings in the ligand are named "C_q-pyrrole". The atoms of the ligand's methyl groups are called "α-Me" and the quaternary carbon atoms to which they are attached "α-C".

NMR spectra were processed and plotted with TopSpin 4.0.7.

High resolution mass spectrometry (HR-MS) was done with the electrospray ionization method (ESI) and with a Bruker ApexQe hybrid 9.4 T FT-ICR.

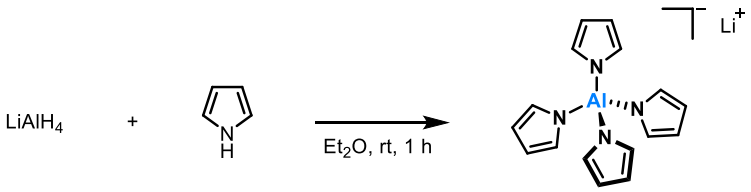
S-2. Preparation of tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato aluminate ([PPh$_4$][1]) and of lithium tetrapyrrolato aluminate

The *meso*-octamethylcalix[4]pyrrolato aluminate ([PPh$_4$][**1**]) was prepared on gram-scale as its tetraphenylphosphonium salt within two steps. The procedures are known to the literature. The obtained substances were characterized by ^{1}H and ^{13}C NMR spectroscopy. Acquired data was found congruent with the values from the literature.



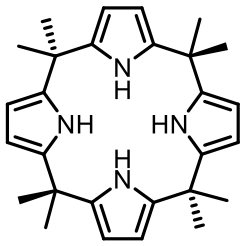
Scheme S-1: Synthesis of tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato aluminate ([PPh$_4$][**1**]).

Lithium tetrapyrrolato aluminate was synthesized in one step from pyrrole and lithium aluminum hydride following a modified procedure taken from the patent of Whitney and Klemann, ExxonMobil Research and Engineering Co (Alkali metal salts of complex anions containing heteroatom substituents and electrolyte compositions containing these, 1978, US4117213A).[1] The obtained material was characterized by ^{1}H and ^{13}C NMR spectroscopy.



Scheme S-2: Synthesis of lithium tetrapyrrolato aluminate.

<u>*meso*-Octamethylcalix[4]pyrrole</u>



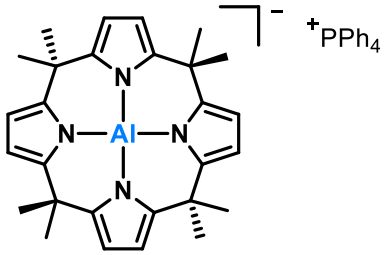
Procedure.[2, 3] In a 500 mL two-necked round-bottom flask equipped with a reflux condenser, acetone (13.0 g, 16.5 mL, 223.6 mmol, 1.0 eq) was dissolved in methanol (160 mL). Pyrrole (15 g, 15.5 mL, 223.6 mmol,

1.0 eq), which was freshly distilled prior to use, was added in one portion. Methanesulfonic acid (4 drops) was added to the colorless solution. The mixture was heated to 60 °C for 3 h. The reaction mixture was allowed to cool down to room temperature, and the solvent was removed under reduced pressure. A pale green solid was obtained as the crude reaction product, which was purified by flash column chromatography on silica gel with dichloromethane/petroleum ether (60:40, R_f = 0.53) as eluent. The solvent was removed from the combined product fractions and *meso*-octamethylcalix[4]pyrrole was obtained as a pale brown solid (13.7 g, 32.0 mmol, 57% yield), which is stable to ambient conditions.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ [ppm] = **7.02** (br s, 4H, N-H), **5.88** (d, $^3J_{HH}$ = 2.8 Hz, 8H, β-H), **1.49** (s, 24H, α-Me).

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ [ppm] = **138.8** (C_q, C_q-pyrrole), **103.1** (CH, β-H), **35.4** (C_q, α-C), **28.9** (CH_3, α-Me).

meso-Octamethylcalix[4]pyrrolato aluminate ([PPh_4][**1**])



[PPh_4][**1**]

Procedure.[4] In a nitrogen-filled glove box, *meso*-octamethylcalix[4]pyrrole (5.00 g, 11.67 mmol, 1.0 eq) and purified (see below) lithium aluminum hydride (1.05 g, 27.62 mmol, 2.4 eq) were dissolved in 1,2-dimethoxyethane (30 mL) in a 500 mL Schlenk flask. An overpressure valve was added, and the reaction mixture was stirred at 95 °C for 48 h. The solvent was removed under reduced pressure and was redissolved in dichloromethane (70 mL). To the pale-yellow solution tetraphenylphosphonium chloride (4.37 g, 11.67 mmol, 1.0 eq), which was dried *in vacuo* at 80 °C for several hours prior to use, was added in one portion, and it was stirred for 1 h at room temperature. The formed colorless precipitate was separated by filtration through a fritted glass filter. The product (7.60 g, 9.61 mmol, 82% yield) was precipitated from its pale-yellow dichloromethane solution by addition of pentane (70 mL). It contains approximately an equimolar amount of dichloromethane. [PPh_4][**1**] was permanently handled under inert conditions.

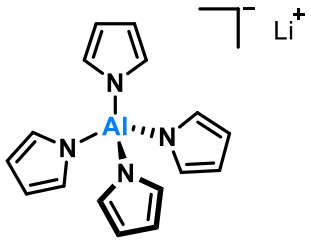
^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.90-7.83** (m, 4H, PPh_4^+), **7.73-7.65** (m, 8H, PPh_4^+), **7.61-7.52** (m, 8H, PPh_4^+), **5.75** (s, 8H, β-H) , **1.64** (s, 12H, α-Me), **1.47** (s, 12H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **147.3** (C_q, C_q-pyrrole), **136.2** (d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **117.8** (d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **100.8** (CH, β-C), **42.6** (C_q, α-C), **35.9** (CH_3, α-Me), **24.8** (CH_3, α-Me).

Procedure for $LiAlH_4$ purification. The commercially available lithium aluminum hydride was purified for the synthesis of [PPh_4][**1**] prior to use. For that, gray $LiAlH_4$ powder (5.0 g) was mixed with diethyl ether (200 mL)

in a 500 mL one-necked Schlenk flask, which was equipped with a Schlenk frit capped with a 250 mL Schlenk flask. The apparatus was flame-dried and flushed with dry argon prior to use. The suspension was stirred for 30 min at room temperature. The gray solid was separated by filtration from the colorless solution. The solvent was removed under reduced pressure to yield a colorless solid (2.9 g) after drying *in vacuo* at 80 °C. The product was used without further characterization and was permanently handled under inert conditions.

Lithium tetrapyrrolato aluminate



Procedure.[1] In a flame-dried 100 mL Schlenk flask, purified lithium aluminum hydride (200 mg, 5.27 mmol, 1.0 eq, for purification procedure see above) was mixed with diethyl ether (10 mL). Freshly distilled pyrrole (366 μL, 354 mg, 5.27 mmol, 1.0 eq) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. The formation of gas was observed. The solvent was removed under reduced pressure, and after drying *in vacuo* the desired product was obtained as a colorless solid. The exact yield was not determined. Lithium tetrapyrrolato aluminate was constantly handled under inert conditions.

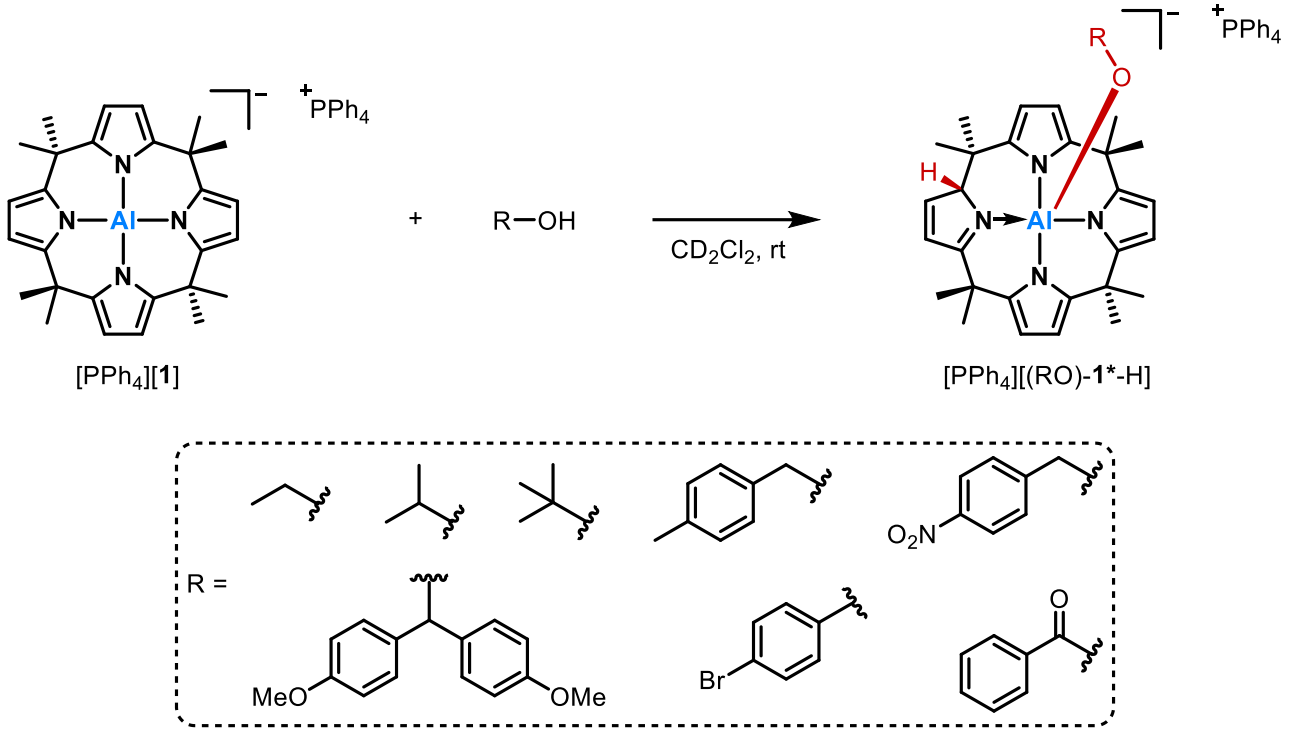
^{1}H NMR (600 MHz, THF-d_8, 295 K), δ [ppm] = **6.69** (s, 8H, H-2/5), **6.00** (s, 8H, H-3/H-4).

^{13}C{^{1}H} NMR (151 MHz, THF-d_8, 295 K), δ [ppm] = **125.7** (CH, C-2/5), **108.3** (CH, C-3/4). Both signals showed somewhat poorly resolved ^{13}C-^{27}Al coupling and appeared, though expected as a sextet ($s_{^{27}Al}$ = 5/2), as doublet-type signals.

^{7}Li NMR (233 MHz, THF-d_8, 295 K), δ [ppm] = 2.45.

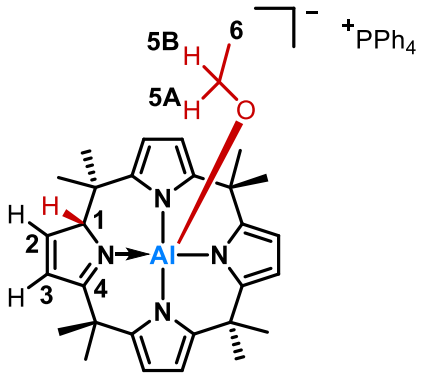
S-3. Addition reactions to [1]$^-$

General Procedure: In a dry nitrogen-filled glovebox, tetraphenylphosphonium *meso*-octamethyl-calix[4]pyrrolato aluminate ([PPh_4][**1**], 10 mg, 12.6 μmol, 1.0 eq) was dissolved in CD_2Cl_2 (0.5 mL). An equimolar amount of the respective alcohol substrate (12.6 μmol, 1.0 eq) was dissolved in CD_2Cl_2 (0.3 mL) and was added to the stirring aluminate solution at room temperature. The reaction mixture turned yellow (orange in the case of *para*-nitrobenzyl alcohol) immediately after the addition of the first drop of the alcohol solution. After complete addition, the solution was transferred to a J. Young NMR tube and was analyzed by NMR spectroscopy. The addition products were also characterized by high resolution electrospray ionization mass spectrometry.



Scheme S-3: Addition reaction of protic substrates to [**1**]$^-$. With ^{t}BuOH, the addition process is not quantitative (see Chapter S-5).

[PPh_4][(EtO)-**1***-H]

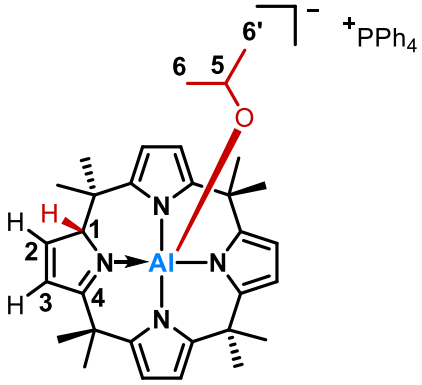


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.92-7.86** (m, 4H, PPh_4^+), **7.75-7.68** (m, 8H, PPh_4^+), **7.62-7.55** (m, 8H, PPh_4^+), **7.56** (1 H, H-2, observed by ^{1}H,^{1}H COSY NMR spectroscopy, expected multiplicity is d), **6.82** (d, $^3J_{HH}$ = 5.1 Hz, 1H, H-3), **5.89** (d, $^3J_{HH}$ = 2.8 Hz, 1H, β-H), **5.83** (d, $^3J_{HH}$ = 2.8 Hz, 1H, β-H), **5.79** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.78** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.70** (d, $^3J_{HH}$ = 2.7 Hz, 1H, β-H), **5.67** (d, $^3J_{HH}$ = 2.7 Hz, 1H, β-H), **5.60** (s, 1H, H-1), **2.73-2.65** (m, 1H, H-5A/5B), **2.43-2.35** (m, 1H, H-5A/5B), **1.75** (s, 3H, α-Me), **1.69** (s, 3H, α-Me), **1.66** (s, 3H, α-Me), **1.63** (s, 3H, α-Me), **1.60** (s, 3H, α-Me), **1.51** (s, 3H, α-Me), **1.32** (s, 3H, α-Me), **0.65** (s, 3H, α-Me), **0.64** (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-6).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **186.9** (C_q, C-4), **156.2** (CH, C-2), **150.9** (C_q, C_q-pyrrole), **150.1** (C_q, C_q-pyrrole), **149.1** (C_q, C_q-pyrrole), **147.0** (C_q, C_q-pyrrole), **146.4** (C_q, C_q-pyrrole), **141.4** (C_q, C_q-pyrrole), **136.2** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **127.4** (CH, C-3), **117.8** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **101.7** (CH, β-C), **101.4** (CH, β-C), **101.0** (CH, β-C), **100.6** (CH, β-C), **100.3** (CH, β-C), **98.2** (CH, β-C), **86.5** (CH, C-1), **55.4** (CH_2, C-5), **40.7** (C_q, α-C), **39.6** (CH_3, α-Me), **38.3** (C_q, α-C), **36.7** (C_q, α-C), **36.6** (C_q, α-C), **36.4** (CH_3, α-Me), **33.4** (CH_3, α-Me), **32.0** (CH_3, α-Me), **28.5** (CH_3, α-Me), **28.0** (CH_3, α-Me), **27.4** (CH_3, α-Me), **26.1** (CH_3, α-Me), **20.5** (CH_3, C-6).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{30}H_{38}AlN_4O$ $[M]^-$: 497.2866, found: 497.2874.

[PPh_4][(^{i}PrO)-**1***-H]

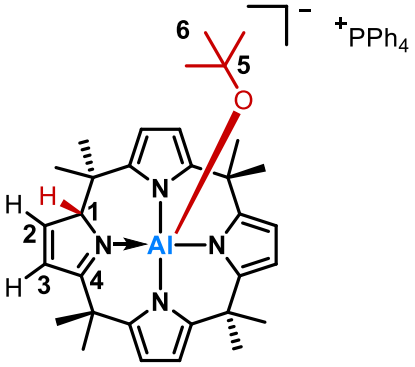


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.92-7.85** (m, 4H, PPh_4^+), **7.76-7.68** (m, 8H, PPh_4^+), **7.62-7.55** (m, 8H, PPh_4^+), **7.56** (d, $^3J_{HH}$ = 5.6 Hz, 1H, H-2), **6.80** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, H-3), **5.90** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.82** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.81** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.77** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.72** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.68** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.66** (s, 1H, H-1), **3.11** (sept, $^3J_{HH}$ = 6.0 Hz, 1H, H-5), **1.75** (s, 3H, α-Me), **1.70** (s, 3H, α-Me), **1.66** (s, 3H, α-Me), **1.63** (s, 3H, α-Me), **1.59** (s, 3H, α-Me), **1.57** (s, 3H, α-Me), **1.27** (s, 3H, α-Me), **0.63** (s, 3H, α-Me), **0.46** (d, $^3J_{HH}$ = 6.0 Hz, 3H, H-6/6'), **0.37** (d, $^3J_{HH}$ = 6.0 Hz, 3H, H-6/6').

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **186.4** (C_q, C-4), **156.5** (CH, C-2), **150.5** (C_q, C_q-pyrrole), **150.4** (C_q, C_q-pyrrole), **149.3** (C_q, C_q-pyrrole), **146.6** (C_q, C_q-pyrrole), **146.2** (C_q, C_q-pyrrole), **141.2** (C_q, C_q-pyrrole), **136.2** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **127.4** (CH, C-3), **117.9** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **102.3** (CH, β-H), **101.08** (CH, β-H), **101.05** (CH, β-H), **101.0** (CH, β-H), **100.6** (CH, β-H), **98.3** (CH, β-H), **85.6** (CH, C-1), **62.5** (CH, C-5), **41.14** (C_q, α-C), **41.09** (C_q, α-Me), **38.1** (C_q, α-C), **37.5** (C_q, α-Me), **36.8** (C_q, α-C), **36.7** (C_q, α-C), **36.4** (C_q, α-Me), **31.1** (C_q, α-Me), **28.9** (C_q, α-Me), **28.0** (C_q, α-Me), **27.2** (C_q, α-Me), **26.9** (CH_3, C-6/6'), **26.7** (CH_3, C-6/6'), **25.3** (C_q, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{31}H_{40}AlN_4O$ $[M]^-$: 511.3023, found: 511.3080.

[PPh_4][(^{t}BuO)-**1***-H]

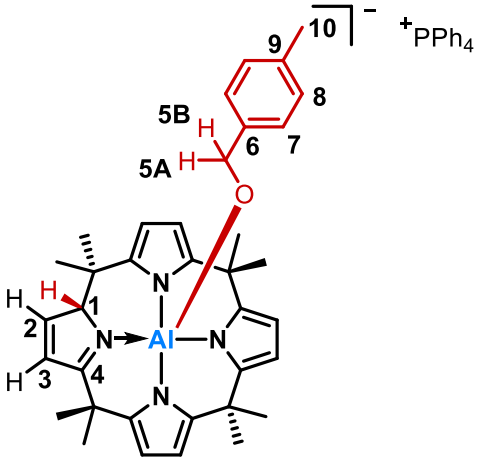


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.91-7.85** (m, 4H, PPh_4^+), **7.75-7.68** (m, 8H, PPh_4^+), **7.62-7.54** (m, 8H, PPh_4^+), **7.57** (1 H, H-2, observed by ^{1}H,^{1}H COSY NMR spectroscopy, expected multiplicity is d), **6.82** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, H-3), **5.90** (s, 1H, H-1), **5.89** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.88** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.82** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.78** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.73** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.69** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **1.75** (s, 3H, α-Me), **1.74** (s, 3H, α-Me), **1.67** (s, 3H, α-Me), **1.63** (s, 3H, α-Me), **1.58** (s, 3H, α-Me), **1.55** (s, 3H, α-Me), **1.21** (s, 3H, α-Me), **0.61** (s, 3H, α-Me), **0.58** (s, 9H, H-6).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **186.3** (C_q, C-4), **156.9** (CH, C-2), **150.9** (C_q, C_q-pyrrole), **150.3** (C_q, C_q-pyrrole), **149.5** (C_q, C_q-pyrrole), **146.6** (C_q, C_q-pyrrole), **146.0** (C_q, C_q-pyrrole), **141.2** (C_q, C_q-pyrrole), **136.2** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **127.8** (CH, C-3), **117.9** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **102.4** (CH, β-C), **101.5** (CH, β-C), **100.8** (CH, β-C), **100.92** (CH, β-C), **100.90** (CH, β-C), **98.7** (CH, β-C), **84.7** (CH, C-1), **68.2** (C_q, C-5), **42.0** (CH_3, α-Me), **41.5** (C_q, α-C), **38.4** (CH_3, α-Me), **38.3** (CH_3, α-Me), **38.1** (C_q, α-C), **36.9** (C_q, α-C), **36.6** (C_q, α-C), **32.4** (CH_3, C-6), **31.0** (CH_3, α-Me), **28.4** (CH_3, α-Me), **28.1** (CH_3, α-Me), **27.0** (CH_3, α-Me), **25.2** (CH_3, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{32}H_{42}AlN_4O$ $[M]^-$: 525.3179, found: 525.3129.

[PPh_4][(*p*-MeBnO)-**1***-H]

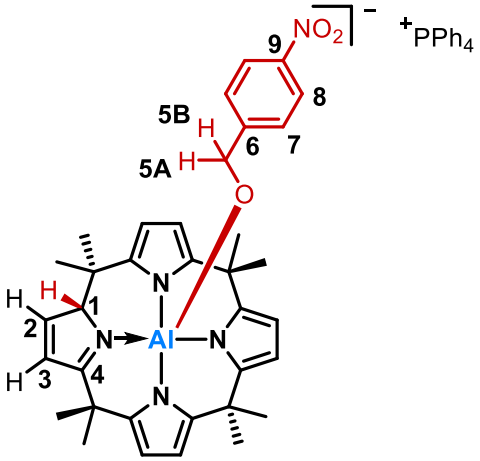


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.90-7.84** (m, 4H, PPh_4^+), **7.74-7.67** (m, 8H, PPh_4^+), **7.60-7.53** (m, 8H, PPh_4^+), **7.48** (d, $^3J_{HH}$ = 5.2 Hz, 1H, H-2), **6.93-6.89** (m, 2H, H-7), **6.89-6.85** (m, 2H, H-8), **6.79** (d, $^3J_{HH}$ = 5.2 Hz, 1H, H-3), **5.90** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.85** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.84** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.80** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.73** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.70** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.54** (s, 1H, H-1), **3.70** (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-5A/5B), **3.14** (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-5A/5B), **2.20** (s, 3H, H-10), **1.74** (s, 3H, α-Me), **1.68** (s, 3H, α-Me), **1.63** (s, 3H, α-Me), **1.60** (s, 3H, α-Me), **1.55** (s, 3H, α-Me), **1.49** (s, 3H, α-Me), **1.34** (s, 3H, α-Me), **0.60** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **186.9** (C_q, C-4), **156.4** (CH, C-2), **151.3** (C_q, C_q-pyrrole), **150.2** (C_q, C_q-pyrrole), **149.2** (C_q, C_q-pyrrole), **147.2** (C_q, C_q-pyrrole), **146.4** (C_q, C_q-pyrrole), **145.3** (C_q, C-6), **141.5** (C_q, C_q-pyrrole), **136.2** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **134.1** (C_q, C-9), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **128.2** (CH, C-8), **127.3** (CH, C-3), **127.0** (CH, C-7), **117.8** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **102.3** (CH, β-C), **101.4** (CH, β-C), **101.2** (CH, β-C), **100.8** (CH, β-C), **100.6** (CH, β-C), **98.0** (CH, β-C), **86.3** (CH, C-1), **62.3** (CH_2, C-5), **40.9** (C_q, α-C), **40.2** (CH_3, α-Me), **38.3** (C_q, α-C), **36.9** (CH_3, α-Me), **36.8** (C_q, α-C), **36.6** (C_q, α-C), **33.7** (CH_3, α-Me), **31.2** (CH_3, α-Me), **28.2** (CH_3, α-Me), **27.6** (CH_3, α-Me), **27.5** (CH_3, α-Me), **25.6** (CH_3, α-Me), **21.1** (CH_3, C-10).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{36}H_{42}AlN_4O$ $[M]^-$: 573.3179, found: 573.3177.

[PPh_4][(*p*-NO_2BnO)-**1***-H]

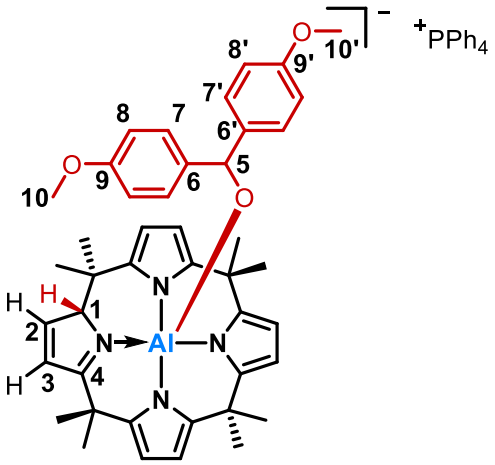


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.92-7.89** (m, 2H, H-8), **7.89-7.85** (m, 4H, PPh_4^+), **7.74-7.67** (m, 8H, PPh_4^+), **7.61-7.55** (m, 8H, PPh_4^+), **7.51** (d, $^3J_{HH}$ = 5.3 Hz, 1H, H-2), **7.23-7.19** (m, 2H, H-7), **6.83** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H-3), **5.87** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.86** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.81** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.75** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.72** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.45** (s, 1H, H-1), **3.82** (d, $^2J_{HH}$ = 15.7 Hz, 1H, H-5A/5B), **3.27** (d, $^2J_{HH}$ = 15.7 Hz, 1H, H-5A/5B), **1.75** (s, 3H, α-Me), **1.69** (s, 3H, α-Me), **1.65** (s, 3H, α-Me), **1.57** (s, 3H, α-Me), **1.56** (s, 3H, α-Me), **1.42** (s, 3H, α-Me), **1.35** (s, 3H, α-Me), **0.60** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **187.4** (C_q, C-4), **157.5** (C_q, C-9), **156.5** (CH, C-2), **151.5** (C_q, C_q-pyrrole), **150.2** (C_q, C_q-pyrrole), **149.0** (C_q, C_q-pyrrole), **147.2** (C_q, C_q-pyrrole), **146.3** (C_q, C-6), **145.9** (C_q, C_q-pyrrole), **141.4** (C_q, C_q-pyrrole), **136.2** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **127.41** (CH, C-3), **127.37** (CH, C-7), **122.8** (CH, C-8), **117.8** (C_q, d, $^1J_{CP}$ = 3.1 Hz, PPh_4^+), **102.6** (CH, β-C), **101.7** (CH, β-C), **101.4** (CH, β-C), **100.9** (CH, β-C), **100.8** (CH, β-C), **98.2** (CH, β-C), **86.4** (CH, C-1), **62.4** (CH_2, C-5), **40.9** (C_q, α-C), **40.0** (CH_3, α-Me), **38.3** (C_q, α-C), **36.9** (CH_3, α-Me), **36.8** (C_q, α-C), **36.6** (C_q, α-C), **33.7** (CH_3, α-Me), **31.2** (CH_3, α-Me), **28.1** (CH_3, α-Me), **27.5** (CH_3, α-Me), **27.3** (CH_3, α-Me), **25.5** (CH_3, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{35}H_{39}AlN_5O_3$ $[M]^-$: 604.2874, found: 604.2886.

[PPh_4][((p-MeOPh)$_2$CHO)-**1***-H]

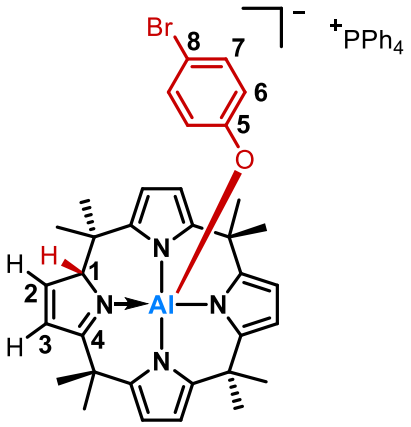


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.91-7.85** (m, 4H, PPh_4^+), **7.75-7.67** (m, 8H, PPh_4^+), **7.62-7.53** (m, 8H, PPh_4^+), **7.35-7.31** (d, $^3J_{HH}$ = 5.2 Hz, 1H, H-2), **7.07-7.02** (m, 2H, H-7/7'), **6.77-6.74** (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, H-3), **6.71-6.67** (m, 2H, H-8/8'), **6.28-6.24** (m, 2H, H-8/8'), **6.22-6.18** (m, 2H, H-7/7'), **5.93** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.84** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.80** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.77** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.70** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.61** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.34** (s, 1H, H-1), **4.20** (s, 1H, H-5), **3.74** (s, 3H, H-10/10'), **3.58** (s, 3H, H-10/10'), **1.77** (s, 3H, α-Me), **1.74** (s, 3H, α-Me), **1.58** (s, 3H, α-Me), **1.41** (s, 3H, α-Me), **1.31** (s, 3H, α-Me), **1.10** (s, 3H, α-Me), **0.94** (s, 3H, α-Me), **0.49** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **186.4** (C_q, C-4), **157.7** (C_q, C-9/9'), **156.8** (C_q, C-9/9'), **156.5** (CH, C-2), **151.6** (C_q, C_q-pyrrole), **151.2** (C_q, C_q-pyrrole), **149.1** (C_q, C_q-pyrrole), **146.1** (C_q, C_q-pyrrole), **146.0** (C_q, C_q-pyrrole), **142.9** (C_q, C-6/6'), **141.7** (C_q, C-6/6'), **141.3** (C_q, C_q-pyrrole), **136.1** (CH, d, $^4J_{CP}$ = 3.1 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **130.2** (CH, C-7/7'), **128.8** (CH, C-7/7'), **127.2** (CH, C-3), **117.8** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **112.7** (CH, C-8/8'), **112.4** (CH, C-8/8'), **103.2** (CH, β-C), **101.34** (CH, β-C), **101.30** (CH, β-C), **101.04** (CH, β-C), **100.97** (CH, β-C), **98.2** (CH, β-C), **85.2** (CH, C-1), **74.4** (CH, C-5), **55.5** (CH_3, C-10/10'), **55.3** (CH_3, C-10/10'), **41.2** (CH_3, α-Me), **41.1** (C_q, α-C), **38.1** (C_q, α-C), **37.9** (CH_3, α-Me), **36.9** (C_q, α-C), **36.4** (C_q, α-C), **35.2** (CH_3, α-Me), **30.5** (CH_3, α-Me), **27.6** (CH_3, α-Me), **27.3** (CH_3, α-Me), **27.2** (CH_3, α-Me), **25.1** (CH_3, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{43}H_{48}AlN_4O_3$ $[M]^-$: 695.3547, found: 695.3561.

[PPh_4][(*p*-BrPhO)-**1***-H]

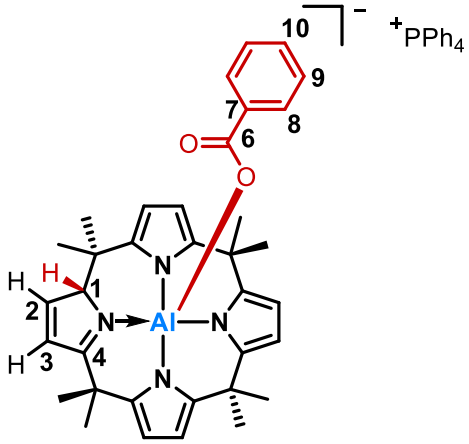


^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.90-7.84** (m, 4H, PPh_4^+), **7.74-7.66** (m, 8H, PPh_4^+), **7.61-7.55** (m, 8H, PPh_4^+), **7.54** (d, $^3J_{HH}$ = 5.2 Hz, 1H, H-2), **6.85** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H-3), **6.75-6.71** (m, 2H, H-7), **5.90** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.89** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.84** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.83** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.73** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.72** (d, $^3J_{HH}$ = 2.9 Hz, 1H, β-H), **5.55-5.51** (m, 2H, H-6), **5.20** (s, 1H, H-1), **1.76** (s, 3H, α-Me), **1.68** (s, 3H, α-Me), **1.66** (s, 3H, α-Me), **1.54** (s, 3H, α-Me), **1.47** (s, 3H, α-Me), **1.41** (s, 3H, α-Me), **1.35** (s, 3H, α-Me), **0.62** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **187.4** (C_q, C-4), **160.6** (C_q, C-5), **156.7** (CH, C-2), **150.4** (C_q, C_q-pyrrole), **150.3** (C_q, C_q-pyrrole), **149.1** (C_q, C_q-pyrrole), **146.8** (C_q, C_q-pyrrole), **146.4** (C_q, C_q-pyrrole), **141.2** (C_q, C_q-pyrrole), **136.2** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.04** (CH, C-7), **131.01** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **127.5** (CH, C-3), **121.6** (CH, C-6), **117.8** (C_q, d, $^1J_{CP}$ = 89.5 Hz, PPh_4^+), **106.8** (C_q, C-8), **103.2** (CH, β-H), **102.1** (CH, β-H), **102.0** (CH, β-H), **101.7** (CH, β-H), **101.4** (CH, β-H), **98.9** (CH, β-H), **85.9** (CH, C-1), **40.9** (C_q, α-C), **40.6** (CH_3, α-Me), **38.3** (C_q, α-C), **37.0** (CH_3, α-Me), **36.7** (C_q, α-C), **36.5** (C_q, α-C), **34.2** (CH_3, α-Me), **31.4** (CH_3, α-Me), **28.7** (CH_3, α-Me), **27.7** (CH_3, α-Me), **27.6** (CH_3, α-Me), **25.5** (CH_3, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{34}H_{37}Al^{79}BrN_4O$ $[M]^-$: 623.1972, found: 623.1980.

[PPh_4][(BzO)-**1***-H]



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.91-7.83** (m, 4H, PPh_4^+), **7.74-7.65** (m, 8H, PPh_4^+), **7.61-7.52** (m, 8H, PPh_4^+), **7.58** (1 H, H-2, observed by ^{1}H,^{1}H COSY NMR spectroscopy, expected multiplicity is d), **7.51-7.46** (m, 2H, H-8), **7.23-19** (m, 1H, H-10), **7.12-7.06** (m, 2H, H-9), **6.87** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H-3), **5.96** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.92** (d, $^3J_{HH}$ = 3.0 Hz, 1H, β-H), **5.81** (d, $^3J_{HH}$ = 3.3 Hz, 1H, β-H), **5.80** (d, $^3J_{HH}$ = 3.3 Hz, 1H, β-H), **5.732** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.728** (d, $^3J_{HH}$ = 3.1 Hz, 1H, β-H), **5.44** (s, 1H, H-1), **1.71** (s, 3H, α-Me), **1.54** (s, 3H, α-Me), **1.53** (s, 3H, α-Me), **1.51** (s, 3H, α-Me), **1.48** (s, 3H, α-Me), **1.46** (s, 3H, α-Me), **1.36** (s, 3H, α-Me), **0.76** (s, 3H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **187.7** (C_q, C-4), **168.2** (C_q, C-6), **155.4** (CH, C-2), **150.3** (C_q, C_q-pyrrole), **149.9** (C_q, C_q-pyrrole), **148.2** (C_q, C_q-pyrrole), **147.0** (C_q, C_q-pyrrole), **146.6** (C_q, C_q-pyrrole), **142.3** (C_q, C_q-pyrrole), **136.9** (C_q, C-7), **136.2** (CH, d, $^4J_{CP}$ = 3.1 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **130.5** (CH, C-10), **130.4** (CH, C-8), **127.8** (CH, C-3), **127.6** (CH, C-9), **117.8** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **102.9** (CH, β-H), **102.0** (CH, β-H), **101.6** (CH, β-H), **101.2** (CH, β-H), **100.12** (CH, β-H), **100.12** (CH, β-H), **87.5** (CH, C-1), **39.2** (Cq, α-C), **38.5** (Cq, α-C), **36.8** (CH_3, α-Me), **36.43** (Cq, α-C),**36.42** (Cq, α-C), **35.5** (CH_3, α-Me), **34.2** (CH_3, α-Me), **30.67** (CH_3, α-Me), **30.65** (CH_3, α-Me), **28.7** (CH_3, α-Me), **28.2** (CH_3, α-Me), **26.6** (CH_3, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for $C_{35}H_{38}AlN_4O_2$ $[M]^-$: 573.2816, found: 573.2839.

S-4. Reactivity of lithium tetrapyrrolato aluminate with ^{i}PrOH

Procedure. In a dry nitrogen-filled glove box, lithium tetrapyrrolato aluminate (7 mg, 23.5 μmol, 1.0 eq) was dissolved in tetrahydrofurane-d_8 (0.6 mL) in a J. Young NMR tube. Subsequently, isopropanol (1.5 mg, 2.0 μL, 26.2 μmol, 1.1 eq) was added at room temperature. No change in color occurred. The reaction was followed by ^{1}H NMR spectroscopy. Immediately after the addition of ^{i}PrOH, the acquired ^{1}H NMR spectrum showed a broad triplet resonance at 9.9 ppm, and one set of additional signals at 6.66 and 6.03 ppm, which is characteristic of pyrrole. Hence, the tetrapyrrolato aluminate readily undergoes alcoholysis and no aluminum-ligand cooperative addition of ^{i}PrOH. This is in stark contrast to the behavior of the calix[4]pyrrolato aluminate.

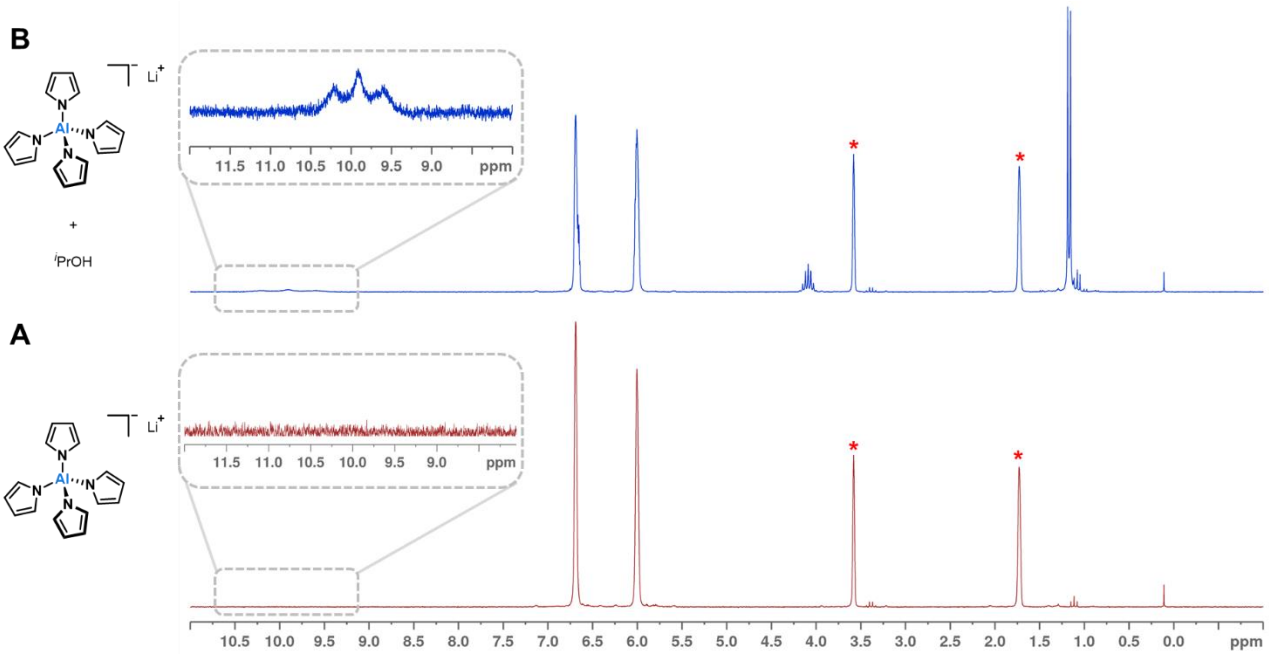
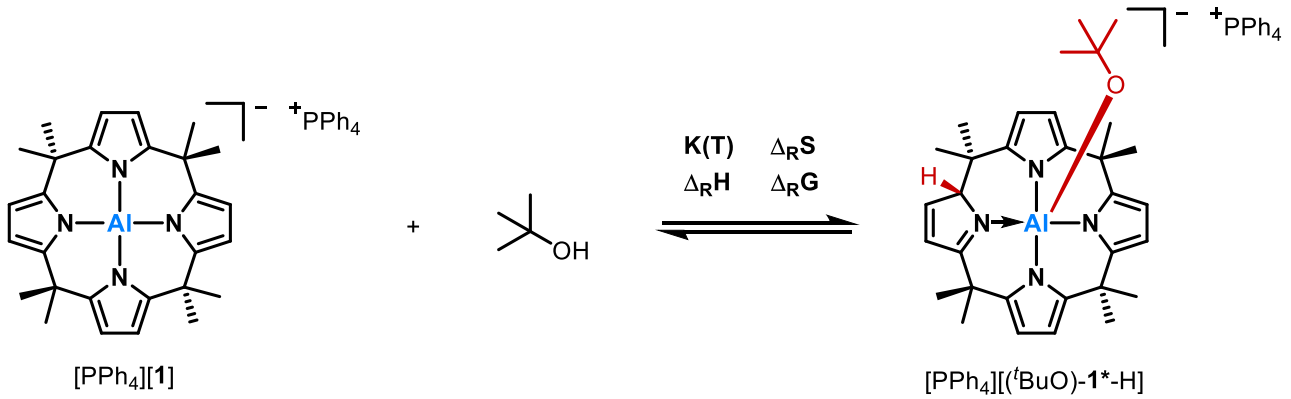


Figure S-1: ^{1}H NMR spectrum (200 MHz, THF-d_8, 298 K) of **A)** [Li][Al(py)$_4$], py = pyrrolato, and of **B)** [Li][Al(py)$_4$] after addition of ^{i}PrOH. The signals of THF-d_7 are marked with red asterisks.

S-5. NMR study of the equilibrium addition reaction with ^{t}BuOH as substrate and removal of the added ^{t}BuOH by reduced pressure

When [PPh_4][**1**] (9.2 mg, 11.6 μmol, 1.0 eq) was treated with an equimolar amount of *tert*-butyl alcohol (0.86 mg, 11.6 μmol, 1.0 eq) in CD_2Cl_2 (617 μL, ρ = 1.362 g cm^{-3}) at room temperature, the ^{1}H NMR spectrum showed the characteristic resonances of the ^{t}BuOH addition product [PPh_4][(^{t}BuO)-**1***-H] beside those of free [PPh_4][**1**] and ^{t}BuOH. To determine the thermodynamic parameters of this equilibrium (Scheme S-4), ^{1}H NMR measurements at variable temperatures were carried out (Figure S-2).



Scheme S-4: Equilibrium addition reaction of ^{t}BuOH to [**1**]$^-$.

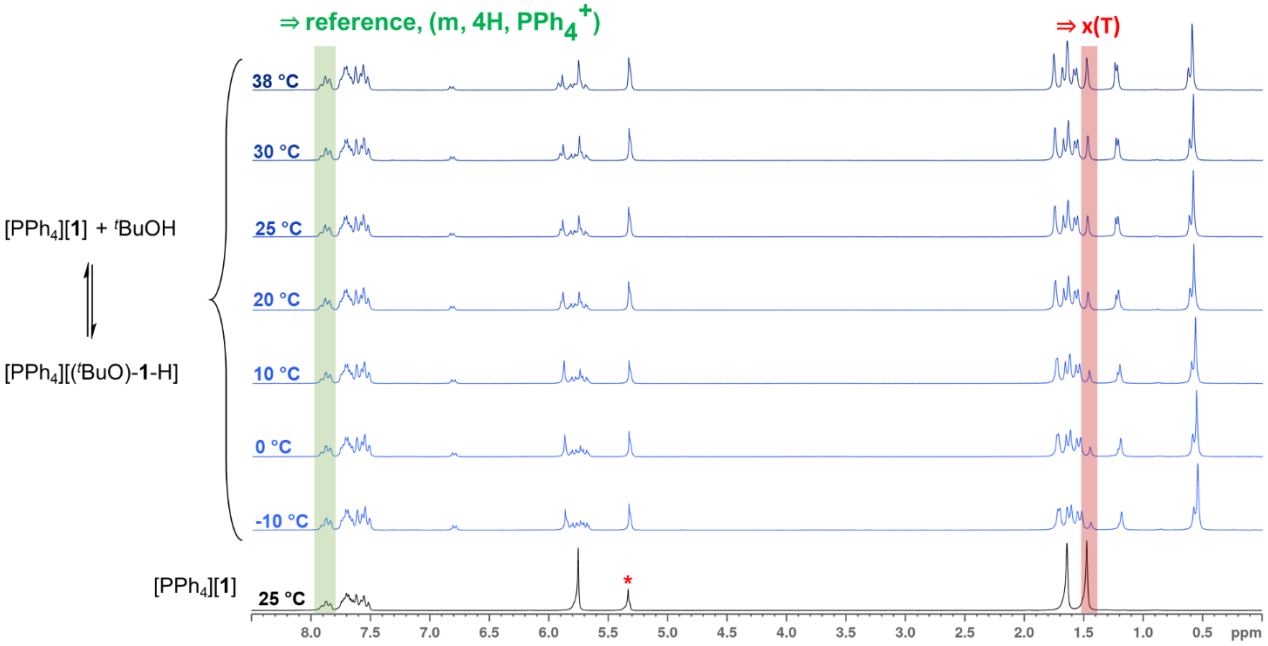


Figure S-2: ^{1}H NMR spectra acquired at variable temperatures (200 MHz, CD_2Cl_2) to study the equilibrium between bound and free ^{t}BuOH. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

The equilibrium constant K(T) for the reaction under investigation (Scheme S-4) is defined as

$$K(T) = \frac{[[PPh_4][(^tBuO)\text{-}\mathbf{1}^*\text{-}H]](T)}{[[PPh_4][\mathbf{1}]](T) \cdot [^tBuOH](T)} \quad \text{(S-1)}$$

and can be simplified to

$$K(T) = \frac{[[PPh_4][\mathbf{1}]]_0 - [[PPh_4][\mathbf{1}]](T)}{\left([[PPh_4][\mathbf{1}]](T)\right)^2} = \frac{1}{x(T)^2 \cdot [[PPh_4][\mathbf{1}]]_0} - \frac{1}{x(T) \cdot [[PPh_4][\mathbf{1}]]_0}. \quad \text{(S-2)}$$

$[[PPh_4][\mathbf{1}]]_0$ is the initial concentration of the aluminate ($[[PPh_4][\mathbf{1}]]_0$ = 9.2 mg / 617 μL = 0.018870 mol L^{-1}) and x(T) the relative amount of free $[PPh_4][\mathbf{1}]$ at a given temperature. The latter is directly accessible through ^{1}H NMR signal integration. One of the methyl singlet resonances of $[PPh_4][\mathbf{1}]$ at 1.46 ppm was used for determining x(T) with the PPh_4^+ multiplet from 7.97-7.81 ppm as the reference (Figure S-2).

With K(T) in hand, a van't Hoff analysis was done relying on

$$K(T) = \exp\left(-\frac{\Delta_R G}{R \cdot T}\right) \quad \text{(S-3)}$$

and

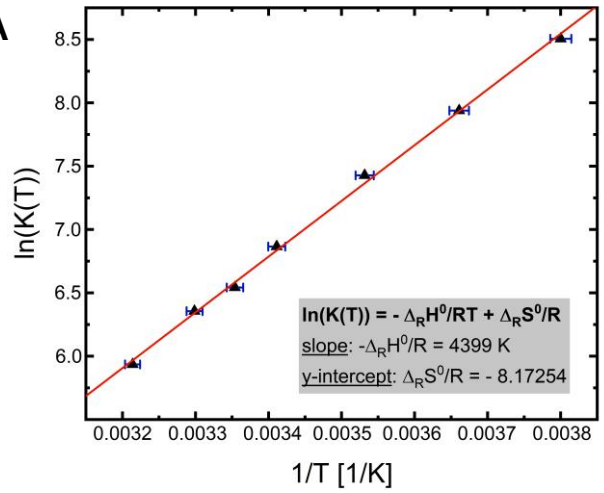
$$\Delta_R G = \Delta_R H - T \cdot \Delta_R S. \quad \text{(S-4)}$$

Combining S-3 and S-4 gives the straight-line equation

$$\ln(K(T)) = -\frac{\Delta_R H}{R} \cdot \frac{1}{T} + \frac{\Delta_R S}{R} \quad \text{(S-5)}$$

which was used to determine $\Delta_R H$ and $\Delta_R S$ and subsequently $\Delta_R G$ with S-4.

A



B

temperature [°C]	relative amount of [**1**]⁻, x(T)
-10	0.098
0	0.128
10	0.163
20	0.209
25	0.241
30	0.261
38	0.311

Figure S-3: A) Van't Hoff plot for the equilibrium given in Scheme S-4. The uncertainty in temperature was estimated to ΔT = 1 °C. As K(T) is influenced by various errors in unidentifiable ways, its uncertainty and the propagation thereof was not considered. **B)** Temperature-dependent relative amount of [**1**]⁻ determined by ^{1}H NMR signal integration (Figure S-2).

Δ_RH = −37 kJ mol^{-1}

Δ_RS = −68 J mol^{-1} K^{-1}

Δ_RG = −16 kJ mol^{-1}

The equilibrium reaction found for ^{t}BuOH was also investigated by DFT calculations (see Chapter S-14). The obtained values are $\Delta_R H_{DFT}$ = −48 kJ mol^{-1} and $\Delta_R G_{DFT}$ = 2 kJ mol^{-1}.

To further investigate the reversibility of the alcohol addition process to [**1**]⁻, a mixture of [PPh$_4$][**1**] (9.0 mg, 11.4 μmol, 1.0 eq) and *tert*-butyl alcohol (2.2 mg, 29.7 μmol, 2.6 eq) in tetrachloroethane-*d*$_2$ (0.8 mL) as solvent was placed in a J. Young NMR tube. The tube was connected to a Schlenk line, and vacuum (approximately 1 mbar) was applied for 90 min at room temperature. After that, most of the solvent was evaporated. The tube was recharged with tetrachloroethane-*d*$_2$ (0.6 mL) and was analyzed by ^{1}H NMR spectroscopy.

It was found that the signals of the ^{t}BuOH addition product ([(^{t}BuO)-**1***-H]⁻) as well as the singlet resonance of free ^{t}BuOH disappeared, and the characteristic signals of [**1**]⁻ appeared in the spectrum. This demonstrates and proves that an added alcohol substrate can be removed from [**1**]⁻, in this example by the application of reduced pressure. The ^{1}H NMR spectrum in Figure S-4B shows a few additional signals with low intensity. They most likely originate from the reaction of [**1**]⁻ with the used solvent tetrachloroethane-*d*$_2$. We also observed reactivity of [**1**]⁻ with tetrachloroethane in previous investigations. However, it was necessary to work with the high-boiling tetrachloroethane-*d*$_2$ to allow for the vacuum application.

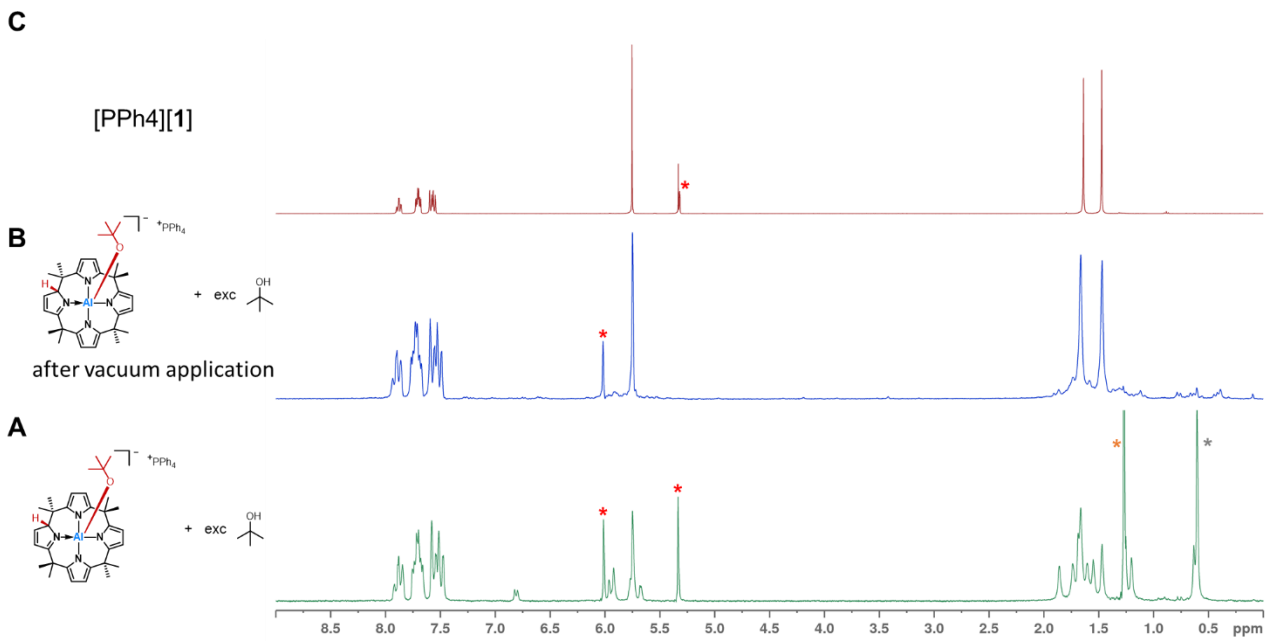
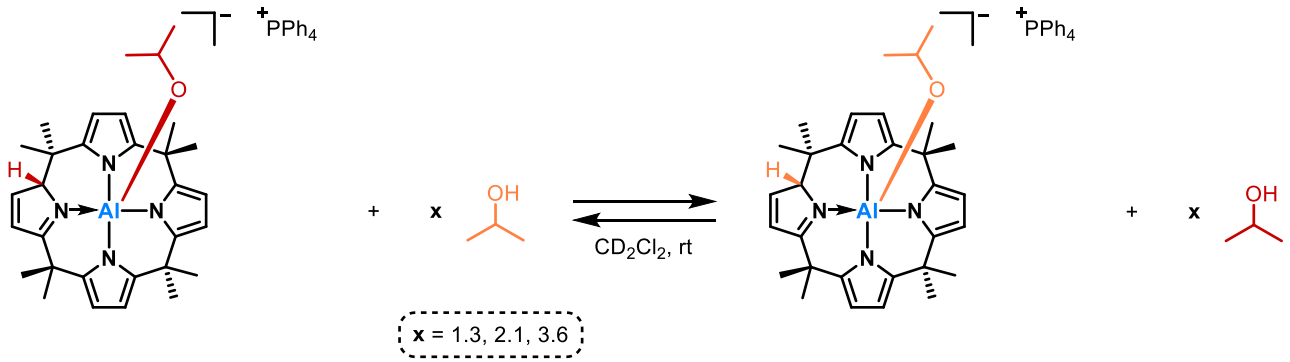


Figure S-4: ^{1}H NMR spectrum (200 MHz, $C_2D_2Cl_4$ (green and blue), 600 MHz, CD_2Cl_2 (red), 298 K), **A)** of a mixture of [PPh_4][**1**] and an excess ^{t}BuOH (2.6 eq), **B)** of the same sample after the application of reduced pressure for 90 min at room temperature, and **C)** of [PPh_4][**1**] for comparison. The signal(s) of $CHDCl_2$, C_2HDCl_4 and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with red asterisks. The signal of free ^{t}BuOH is marked with an orange, that of bound ^{t}BuOH with a gray asterisk. The spectra collected with $C_2D_2Cl_4$ were referenced using the pyrrole resonance of [**1**]$^{-}$ at 5.75 ppm (in CD_2Cl_2).

S-6. ^{1}H,^{1}H EXSY NMR measurements

The self-exchange of isopropanol at [**1**]$^{-}$ (Scheme S-5) was studied by ^{1}H,^{1}H exchange NMR spectroscopy (^{1}H,^{1}H EXSY NMR[5]). This technique gives access to chemical rate constants k by integration of cross and diagonal peaks in a series of ^{1}H,^{1}H NOESY NMR spectra. Samples were prepared by dissolving [PPh_4][**1**] (9.2 mg, 11.6 μmol, 1.0 eq) in CD_2Cl_2 (889.7 mg, 653 μL, ρ = 1.362 g cm^{-3}) and subsequent addition of an excess of isopropanol. The exact amount of added ^{i}PrOH (2.3, 3.1, and 4.6 eq relative to [PPh_4][**1**]) was determined by ^{1}H NMR signal integration.



Scheme S-5: Self-exchange reaction of isopropanol at [**1**]$^{-}$.

The samples were then analyzed by ^{1}H,^{1}H NOESY NMR spectroscopy with varying mixing times d8 (d8 = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1.0, and 2.0 s). For each sample, a separate reference data set was acquired with d8 = 0.00275 s.

To ensure accurate integration values, prior to the NOESY NMR experiments, the spin lattice relaxation times (T_1) of the involved nuclei within their chemical environment were estimated with a ^{1}H inversion recovery experiment. The free isopropanol was found limiting. An interpuls delay time of 4 s resulted in complete recovery of all signals including those of free ^{i}PrOH. Compromising between the required time for data acquisition and the desired accuracy of the data, the delay time (d1) for the ^{1}H,^{1}H NOESY NMR experiments was set to d1 = 20 s (3.5 T_1).

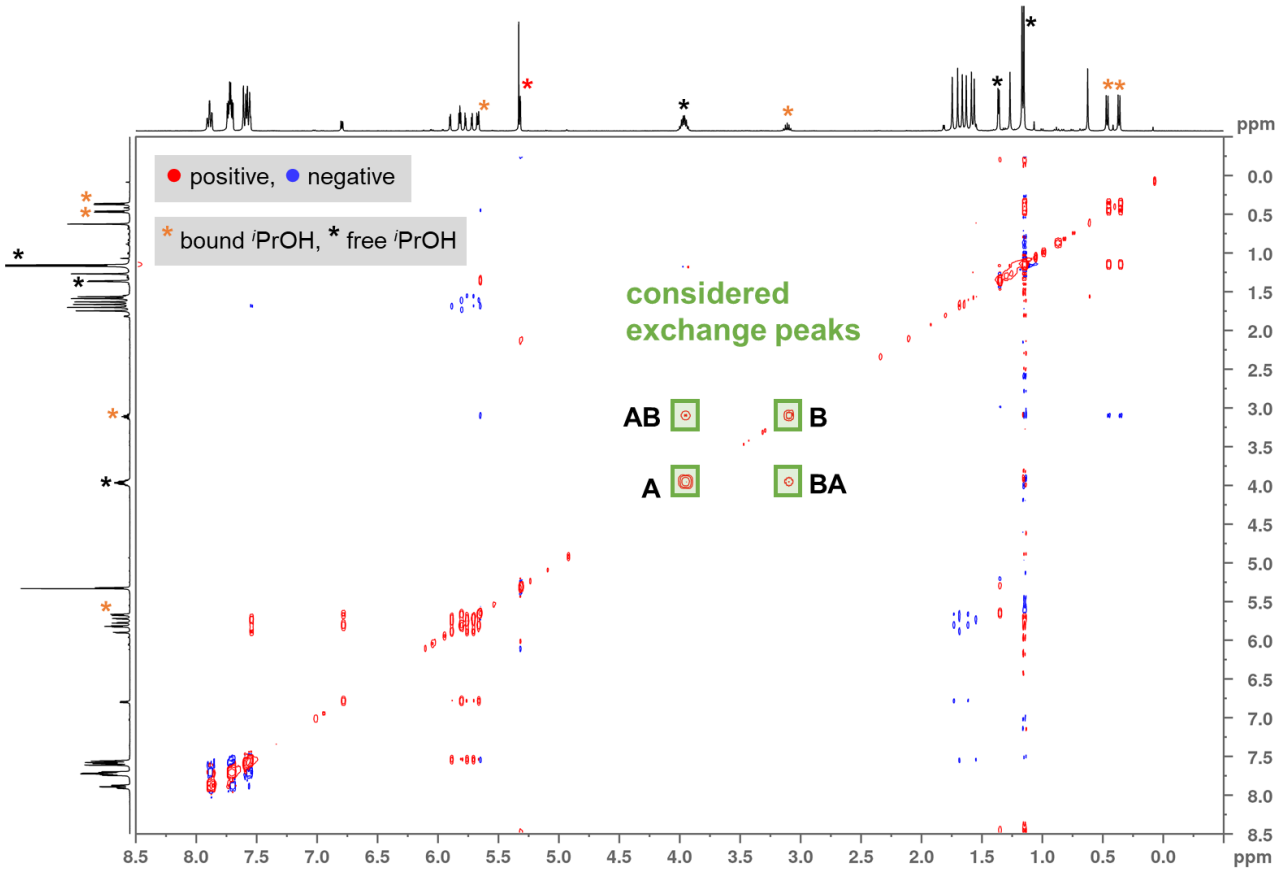


Figure S-5: Exemplary ^{1}H,^{1}H NOESY NMR spectrum (400 MHz, CD_2Cl_2, 298 K, d1 = 20 s, d8 = 2 s) which were acquired for the EXSY NMR experiments of [**1**]$^-$ in the presence of an excess of isopropanol. The signals of the methine group of the bound and free isopropanol (A, B, AB, BA) were used for evaluation. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

The obtained spectra were evaluated by cross and diagonal peak integration. The signals of the methine H of free and bound isopropanol were used as they are well separated from each other as well as from other potentially overlapping signals. The integrals were referenced against the A integration value (Figure S-5) of the measurements with d8 = 0.00275 s. The obtained normalized values for the cross peaks AB_{norm}, BA_{norm} were averaged to obtain the typical 2D-EXSY curves. The uncertainty introduce by the averaging was estimated by calculating[6]

$$\Delta\left[\left(\frac{AB_{norm} + BA_{norm}}{2}\right)\right] = \frac{|AB_{norm} - BA_{norm}|}{2}. \qquad \text{(S-6)}$$

The 2D-EXSY curves are the averaged relative signal cross peak intensities plotted against the mixing times (Figure S-6).

Table S-1: Integral values extracted from the respective $^{1}H,^{1}H$ NOESY NMR spectra. For the assignment of the given integral areas A, B, AB, and BA see Figure S-5. $\Delta[(AB_{norm}+BA_{norm})/2]$ denotes the estimated error of the averaged cross peak integrals which was calculated following equation S-6.

mixing time, d8 [s]	A_{norm}	B_{norm}	AB_{norm}	BA_{norm}	$(AB_{norm}+BA_{norm})/2$	$\Delta[(AB_{norm}+BA_{norm})/2]$
2.3 eq of ^{i}PrOH						
0.00275	1	0.82949	-0.00035	0.00376	0.00171	0.0021
0.1	0.95620	0.76821	0.00547	0.00974	0.00761	0.0021
0.2	0.93464	0.71661	0.02014	0.01689	0.01852	0.0016
0.3	0.91472	0.66539	0.02606	0.02471	0.02539	0.0007
0.4	0.89351	0.62396	0.03575	0.02873	0.03224	0.0035
0.5	0.87562	0.58604	0.03900	0.03658	0.03779	0.0012
0.6	0.85834	0.54747	0.04526	0.04224	0.04375	0.0015
1.0	0.79925	0.42665	0.06491	0.05891	0.06191	0.0030
2.0	0.68794	0.23266	0.08916	0.08319	0.08618	0.0030
3.1 eq of ^{i}PrOH						
0.00275	1	0.55601	0.00124	0.00046	0.00085	0.0003
0.1	0.83989	0.44390	0.00390	0.00530	0.00460	0.0007
0.2	0.94760	0.47830	0.01209	0.01036	0.01123	0.0009
0.3	0.93418	0.44656	0.01900	0.01625	0.01763	0.0014
0.4	0.92254	0.41758	0.02519	0.01975	0.02247	0.0027
0.5	0.90495	0.38983	0.02885	0.02306	0.02596	0.0029
0.6	0.89325	0.36667	0.03283	0.02788	0.03036	0.0025
1.0	0.74878	0.24792	0.04023	0.03547	0.03785	0.0024
2.0	0.77697	0.15278	0.06642	0.05734	0.06188	0.0045
4.6 eq of ^{i}PrOH						
0.00275	1	0.37307	0.00250	0.00190	0.00220	0.0003
0.1	0.96628	0.33963	0.00489	0.00446	0.00468	0.0002
0.2	0.94982	0.31750	0.00791	0.00615	0.00703	0.0009
0.3	0.94611	0.29637	0.01225	0.00988	0.01107	0.0012
0.4	0.93450	0.27773	0.01545	0.01227	0.01386	0.0016
0.5	0.92675	0.26065	0.01890	0.01462	0.01676	0.0021
0.6	0.91912	0.24376	0.02221	0.01716	0.01969	0.0025
1.0	0.89490	0.18900	0.03240	0.02453	0.02847	0.0039
2.0	0.84481	0.10122	0.04652	0.03539	0.04096	0.0056

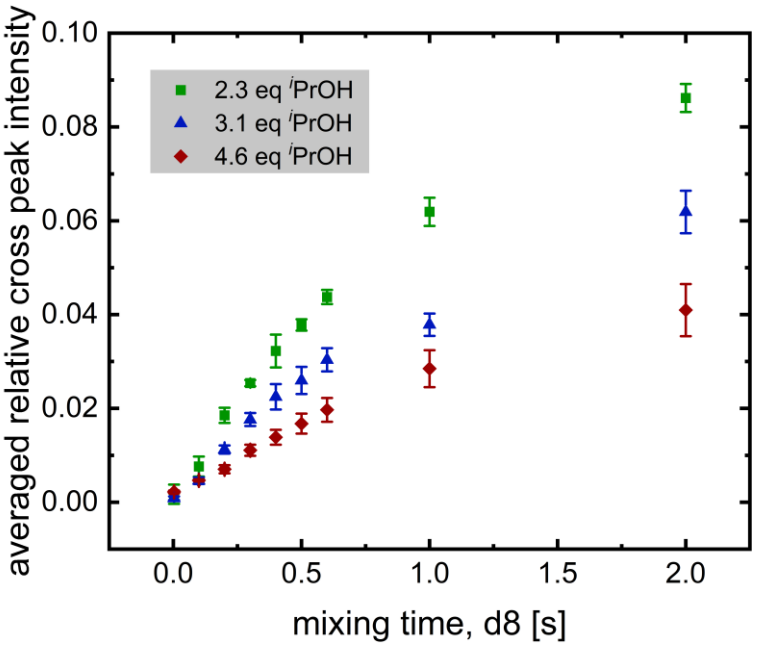


Figure S-6: ^{1}H,^{1}H EXSY NMR plot based on the data given in Table S-1.

For quantitative evaluation, the collected 2D-EXSY data was subjected to a matrix evaluation technique as it was proposed by Perrin and Gipe[7, 8] based on previous work from Macura and Ernst[9]. It solves the fundamental equation S-7, which relates the cross and diagonal peak intensities I_{ij}, the equilibrium magnetization M_j^0, the mixing time d8, and the desired rate matrix **R** by

$$I_{ij} = M_j^0 \cdot \left(e^{-\mathbf{R} \cdot d8}\right)_{ij}. \tag{S-7}$$

The components of **R** can be obtained by calculating

$$\mathbf{R} = -\frac{\ln \mathbf{A}}{d8} = -\frac{\mathbf{X}\,(\ln \Lambda)\,\mathbf{X}^{-1}}{d8}. \tag{S-8}$$

The matrix **A** contains the normalized peak intensities which are directly obtainable through diagonal and cross peak integration:

$$A_{ij} = \frac{I_{ij}}{M_j^0}. \tag{S-9}$$

X is the eigenvector matrix of **A**. That means

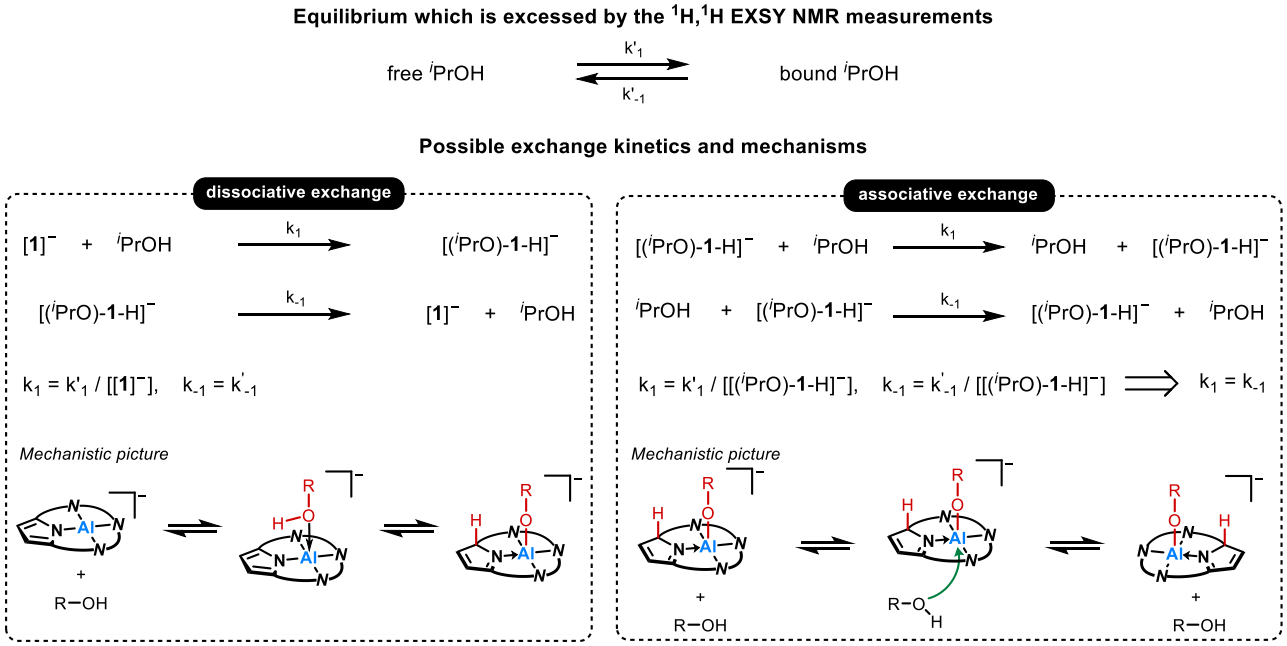
$$\mathbf{X}^{-1}\mathbf{A}\mathbf{X} = \Lambda = \mathrm{diag}(\lambda_i) \tag{S-10}$$

and

$$\ln(\mathbf{\Lambda}) = \mathrm{diag}(\lambda_i). \qquad \text{(S-11)}$$

λ_i are the eigenvalues of **A**.

This mathematical scheme is implemented in the Mestrelab Research EXSY evaluation applet EXSYCalc, which was used for calculating the magnetization exchange rates k'. These are the off-diagonal elements of **R**, which is a 2x2 matrix for the here studied problem. The magnetization exchange rates k' can be directly related to the chemical reaction rates k by considering an appropriate kinetic model. For the self-exchange of isopropanol at $[\mathbf{1}]^-$ (Scheme S-5), two kinetic models can be imagined – a dissociative or an associative mechanism (Scheme S-6).



Scheme S-6: Hypotheses for the kinetic scheme of the self-exchange of ^{i}PrOH at $[\mathbf{1}]^-$.

The dissociative hypothesis implies that k_{-1} is not dependent on the concentration of the excess free ^{i}PrOH – in contrast to k_1 which depends on the added amount of isopropanol. It also implies that $k_{-1} = k'_{-1}$ as the dissociation is a first order reaction. In the associative picture, the forward and the backward reaction are identical ($k_1 = k_{-1}$), hence also equally dependent on the free ^{i}PrOH concentration. So, the question was addressed whether and if so, how k_{-1} and k'_{-1} are changing when varying the amount of added ^{i}PrOH.

With EXSYCalc, for each ^{i}PrOH concentration and for each mixing time d8 the magnetization exchange rates k' were calculated and averaged. The obtained numbers are plotted against the amount of added ^{i}PrOH (Figure S-7). The uncertainty of $\bar{k}'$ was calculated based on equation S-12.

$$\Delta\bar{k}' = \sqrt{\frac{\sum_{i=1}^{n}\left(k_i' - \bar{k}'\right)^2}{n \cdot (n-1)}},\ n=8. \qquad \text{(S-12)}$$

Table S-2: Magnetization exchange rates calculated for the individual mixing times d8.

mixing time, d8 [s]	0.1	0.2	0.3	0.4	0.5	0.6	1.0	2.0	$\bar{k}'$	$\Delta\bar{k}'$
2.3 eq of ^{i}PrOH										
$k'_{1\_2.3}$ [s]	0.104	0.094	0.096	0.088	0.093	0.093	0.091	0.093	**0.094**	**0.002**
$k'_{-1\_2.3}$ [s]	0.070	0.135	0.122	0.131	0.119	0.121	0.122	0.120	**0.118**	**0.007**
3.1 eq of ^{i}PrOH										
$k'_{1\_3.1}$ [s]	0.065	0.057	0.062	0.059	0.058	0.060	0.061	0.060	**0.060**	**0.001**
$k'_{-1\_3.1}$ [s]	0.086	0.120	0.131	0.136	0.130	0.128	0.124	0.125	**0.123**	**0.006**
4.6 eq of ^{i}PrOH										
$k'_{1\_4.6}$ [s]	0.048	0.034	0.038	0.037	0.036	0.037	0.036	0.035	**0.038**	**0.002**
$k'_{-1\_4.6}$ [s]	0.140	0.118	0.126	0.124	0.126	0.127	0.127	0.124	**0.126**	**0.002**

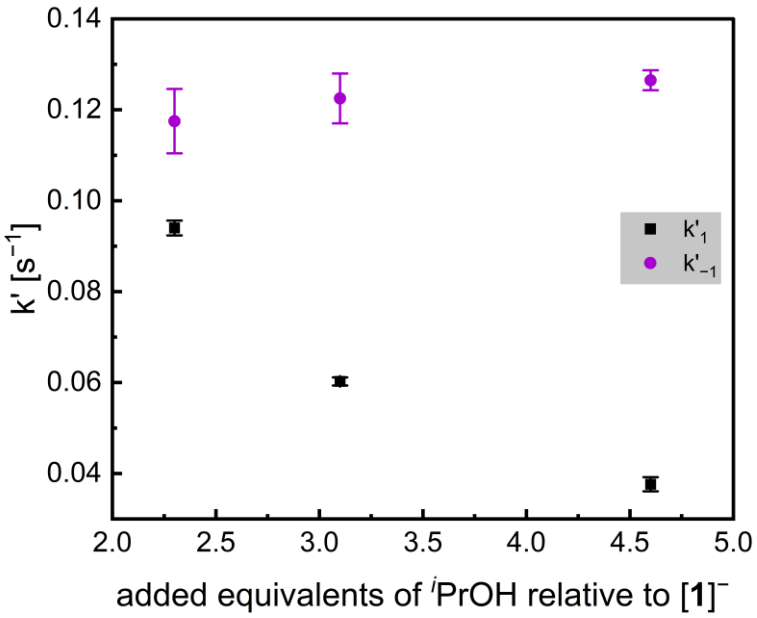


Figure S-7: Mean magnetization exchange rates k' plotted against the added equivalents of ^{i}PrOH relative to [**1**]$^-$.

It is found that k'_1 is decreasing with an increasing amount of added ^{i}PrOH; k'_{-1} remains constant, within the error margins. This is a strong argument against the associative mechanism, which demands for the identical influence of the ^{i}PrOH concentration on both rate constants. $k'_{-1} = k_{-1}$ stays constant which is consistent with the dissociative mechanism. The surprising fact that k'_1 is decreasing with an increasing free ^{i}PrOH concentration remains unanswered. However, it is not of importance for qualitatively distinguishing between the associative and the dissociative path.

The three k_{-1} values were averaged and the mean value (k_{obs}) was used to estimate the Gibbs free activation energy $\Delta_R G^{\ddagger}$ at 298.15 K for the release of isopropanol from [**1**]$^-$ by following

$$\Delta_R G^{\ddagger} = -R \cdot T \cdot \ln\left(\frac{k_{obs} \cdot h}{\kappa \cdot k_B \cdot T}\right), \kappa = 1, \qquad \text{(S-13)}$$

with

$$\Delta(\Delta_R G^{\ddagger}) = \frac{R \cdot T}{k_{obs}} \cdot \Delta k_{obs}. \qquad \text{(S-14)}$$

$$k_{obs} = (0.122 \pm 0.009)\ s^{-1}$$

$$\Delta_R G^{\ddagger} = (78.2 \pm 0.2)\ kJ\ mol^{-1}$$

The two exchange mechanisms were also analyzed by DFT calculations (see Chapter S-14). The Gibbs free activation energies for the two transition states of the dissociative path were calculated to $\Delta_R G^{\ddagger}_{TS\text{-}A}$ = 40.3 kJ mol^{-1} and $\Delta_R G^{\ddagger}_{TS\text{-}B}$ = 62.6 kJ mol^{-1}.

S-7. Deuterium labeling experiments

Three deuterium labeling experiments were carried out with ethanol-*d*$_1$ (EtOD, ρ = 0.806 g cm^{-3}). First, [PPh$_4$][**1**] (9 mg, 11.4 μmol, 1.0 eq) was reacted with ethanol-*d*$_1$ (1.13 μL, 19.3 μmol, 1.7 eq) in CH_2Cl_2 (0.6 mL). The reaction was followed over time by ^{1}H NMR spectroscopy. The singlet resonance at 5.60 ppm (transferred proton) was found increasing, whereas all signals of the pyrrolic protons (β-protons) decreased (Figure S-8, S-9).

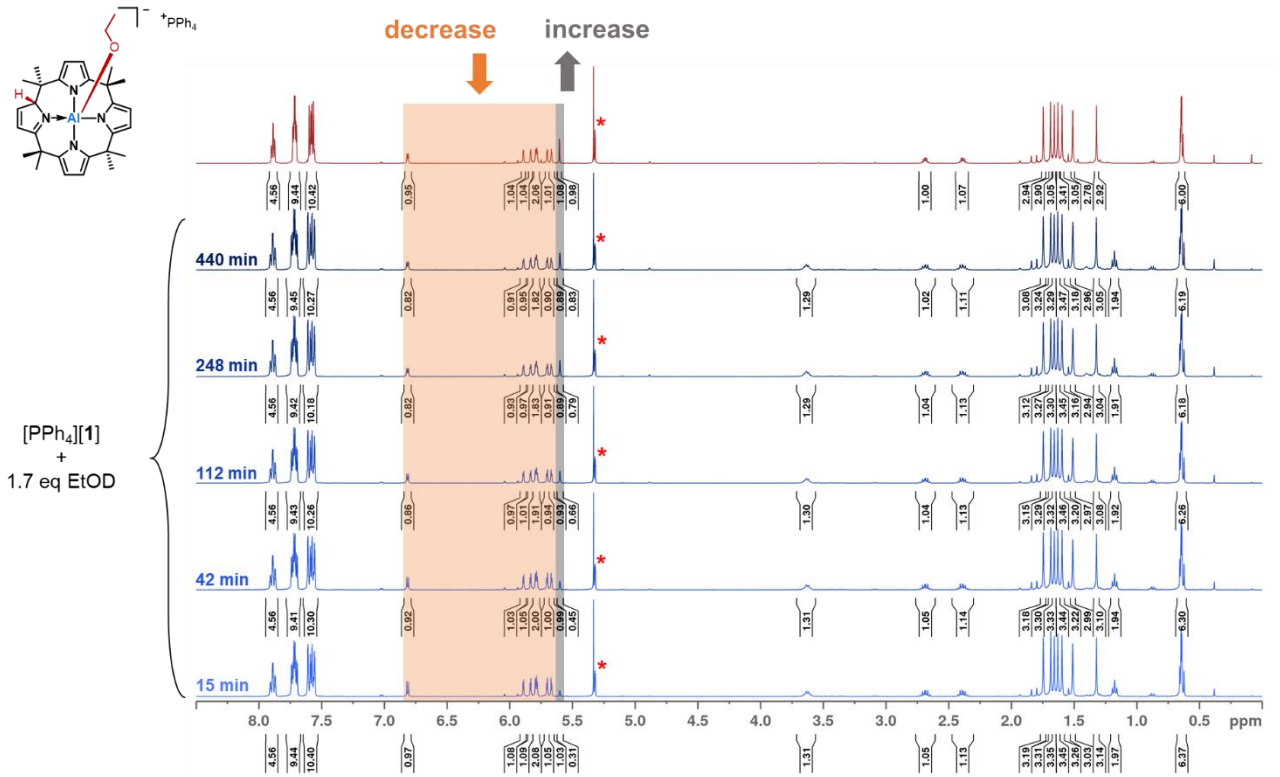


Figure S-8: ^{1}H NMR spectra (400 MHz, 600 MHz (only red spectrum), CD_2Cl_2, 298 K) of a sample of [PPh$_4$][**1**] treated with EtOD. The given times are the elapsed times after EtOD addition. Red spectrum: ^{1}H NMR spectrum of [PPh$_4$][(EtO)-**1***-H] for comparison. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh$_4$][**1**], are marked with a red asterisk.

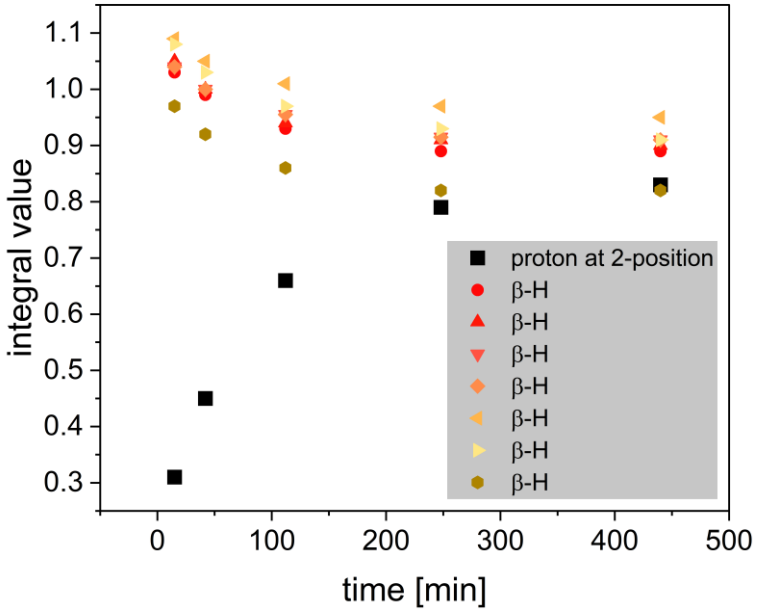


Figure S-9: Integral values extracted from the spectra shown in Figure S-8 plotted against the time after EtOD addition.

Second, [PPh_4][**1**] (9 mg, 11.4 μmol, 1.0 eq) was treated with a slight excess of ethanol-d_1 (0.75 μL, 12.8 μmol, 1.1 eq) in CH_2Cl_2 (0.6 mL). The sample was analyzed by ^{2}H NMR spectroscopy several hours after EtOD addition. The obtained result resembles the aromatic region of the ^{1}H NMR spectrum of [(EtO)-**1***-H]$^-$ acquired in CD_2Cl_2. Hence, the deuterium label is statistically distributed over all possible nine backbone positions. This is a strong indication for the addition of EtOH(D) to [**1**]$^-$ to be reversible and proves the H/D scrambling within [PPh_4][(EtO)-**1***-H(D)].

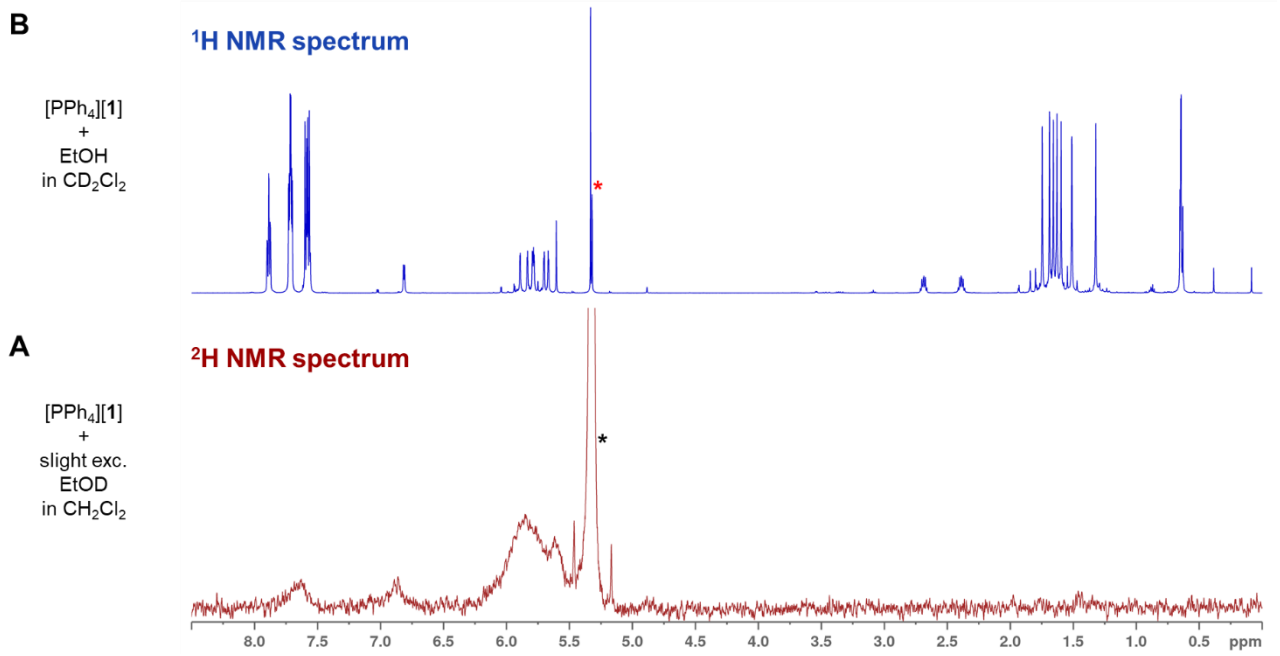
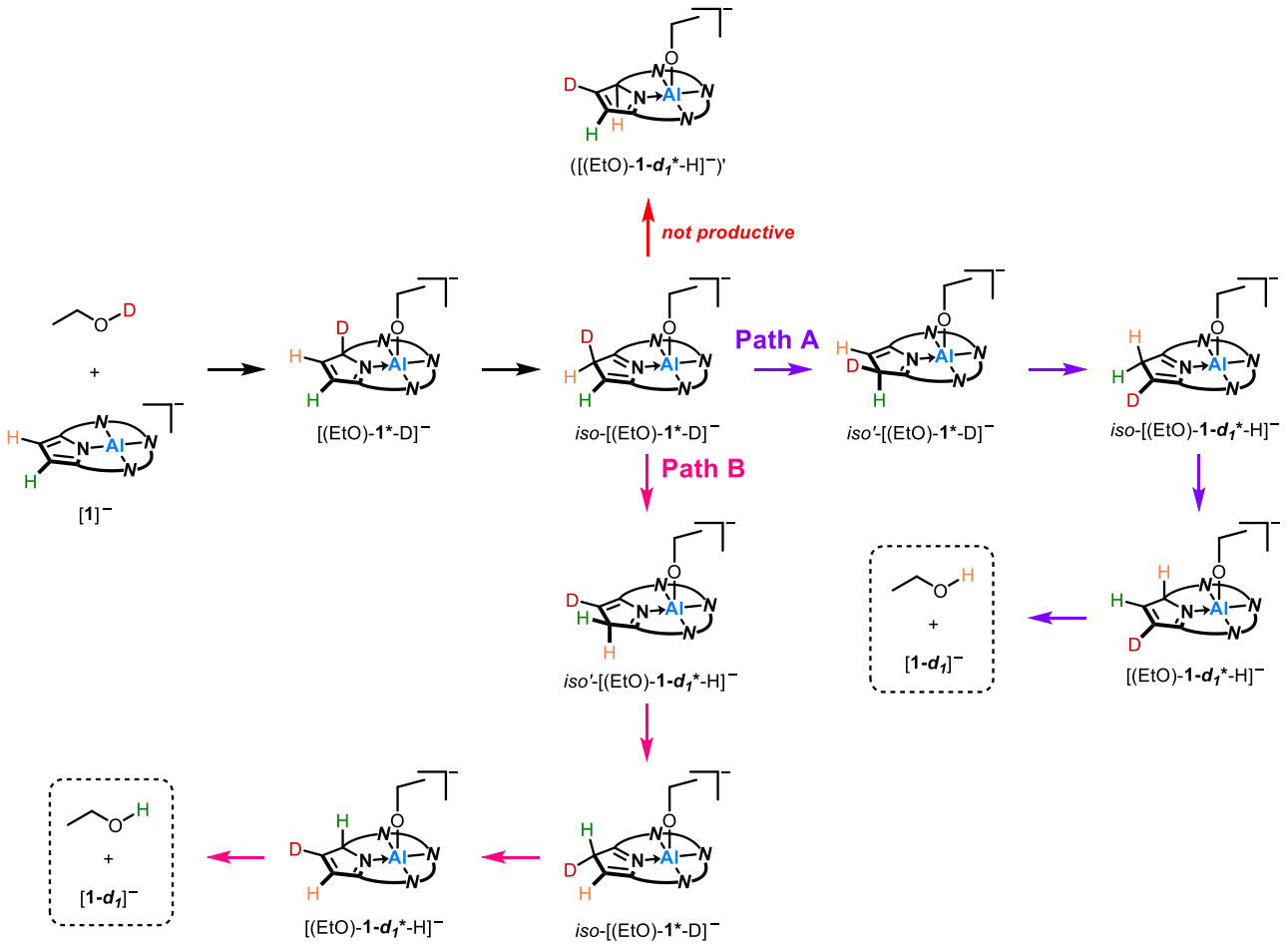


Figure S-10: A) ^{2}H NMR spectrum (92 MHz, CH_2Cl_2, 298 K) of [PPh4][**1**] treated with a slight excess of EtOD. To the sample was added as a reference 0.5 μL CD_2Cl_2 (black asterisk). **B)** ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of [PPh4][(EtO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

Mechanism. For the H/D scrambling mechanism, we propose a series of [1,5]H/D sigmatropic shiftings (Scheme S-7). First, ethanol-d_1 undergoes the addition reaction to [**1**]$^-$ and [(EtO)-**1***-D]$^-$ is formed. From there, thermally allowed [1,5]H/D sigmatropic shiftings proceed in a suprafacial manner, that is, the shifting H or D remains on the same side of the pyrrole ring. To ensure that the observed scrambling is a thermally driven reaction, the first reaction mentioned above was repeated under the exclusion of light. The same scrambling was found. Hence, in [(EtO)-**1***-D]$^-$, a thermal [1,5]D sigmatropic rearrangement takes place to give *iso*-[(EtO)-**1***-D]$^-$. This compound can undergo four further sigmatropic rearrangements. First, the reaction back to [(EtO)-**1***-D]$^-$ which is of course not productive. Also not productive is a sigmatropic shift of a proton to the 2-position of the dearomatized pyrrole ring but *trans* to the bound alkoxo substituent (([(EtO)-**1-*d*$_1$***-H]$^-$)'). This would deny alcohol dissociation from [**1**]$^-$.

However, two additional pathways are productive. Both of which include the formation of an *iso'* tautomer that is either formed through a [1,5]D sigmatropic shift (path A, *iso'*-[(EtO)-**1***-D]$^-$) or through a [1,5]H sigmatropic shift (path B, *iso'*-[(EtO)-**1-*d*$_1$***-H]$^-$). Path A is completed by the reformation of the *iso* tautomer by a H sigmatropic shift (*iso*-[(EtO)-**1-*d*$_1$***-H]$^-$) and subsequent transfer of a proton to the 2-position of the pyrrole ring which gives [(EtO)-**1-*d*$_1$***-H]$^-$. Now, EtOH can be eliminated from the aluminate, and [**1-*d*$_1$**]$^-$ is obtained. Similarly, in path B, *iso'*-[(EtO)-**1-*d*$_1$***-H]$^-$ undergoes a sigmatropic rearrangement to *iso*-[(EtO)-**1***-D]$^-$ that is also capable of delivering a proton to the 2-position of the dearomatized pyrrole ring. The thereby obtained [(EtO)-**1-*d*$_1$***-H]$^-$ eliminates EtOH, and [**1-*d*$_1$**]$^-$ is formed. These cascades of [1,5]H/D sigmatropic shiftings allow for the statistical distribution of the deuterium label introduced by EtOD.

A full quantum chemical investigation of the reaction pathways shown in Scheme S-7 was carried out. The obtained results support the proposed mechanism and are presented in Chapter 15.



Scheme S-7: Proposed mechanism for the H/D scrambling observed in [**1**]$^-$ when treated with EtOD.

Third, it was also tested to which degree the β-protons in [**1**]$^-$ can be exchanged against deuterium atoms by the described mechanistic scenario, that is alcohol addition and H/D scrambling *via* [1,5]H/D sigmatropic rearrangements. For that, [PPh_4][**1**] (9 mg, 11.4 μmol, 1.0 eq) was treated with ethanol-*d*$_1$ (23.90 μL, 409.6 μmol, 36.0 eq) in CD_2Cl_2 (0.6 mL). After 24 h at room temperature, the sample was analyzed by electrospray ionization mass spectrometry. The thereby obtained results gave significantly more inside compared to the results obtained by ^{1}H NMR spectroscopy. Under the applied ESI-MS conditions, the alcohol addition products always underwent dissociation to a certain degree. This dissociation was especially pronounced with ethanol as substrate. So the detected peaks of free [**1-*d*$_x$**]$^-$ were used for evaluation (Figure S-11). The data of interest is:

Table S-3: Molecular formulas and the corresponding exact masses of the individual [**1-*d*$_x$**]$^-$, x = 0, 1, 2, 3, 4, 5, 6, 7, 8.

compound	molecular formula	exact mass [u]
[**1-*d*$_0$**]$^-$	$C_{28}H_{32}AlN_4$	451.2448
[**1-*d*$_1$**]$^-$	$C_{28}H_{31}D_1AlN_4$	452.2511
[**1-*d*$_2$**]$^-$	$C_{28}H_{30}D_2AlN_4$	453.2573
[**1-*d*$_3$**]$^-$	$C_{28}H_{29}D_3AlN_4$	454.2636
[**1-*d*$_4$**]$^-$	$C_{28}H_{28}D_4AlN_4$	455.2699
[**1-*d*$_5$**]$^-$	$C_{28}H_{27}D_5AlN_4$	456.2762

$[\mathbf{1}\text{-}d_6]^-$	$C_{28}H_{26}D_6AlN_4$	457.2824
$[\mathbf{1}\text{-}d_7]^-$	$C_{28}H_{25}D_7AlN_4$	458.2887
$[\mathbf{1}\text{-}d_8]^-$	$C_{28}H_{24}D_8AlN_4$	459.2950

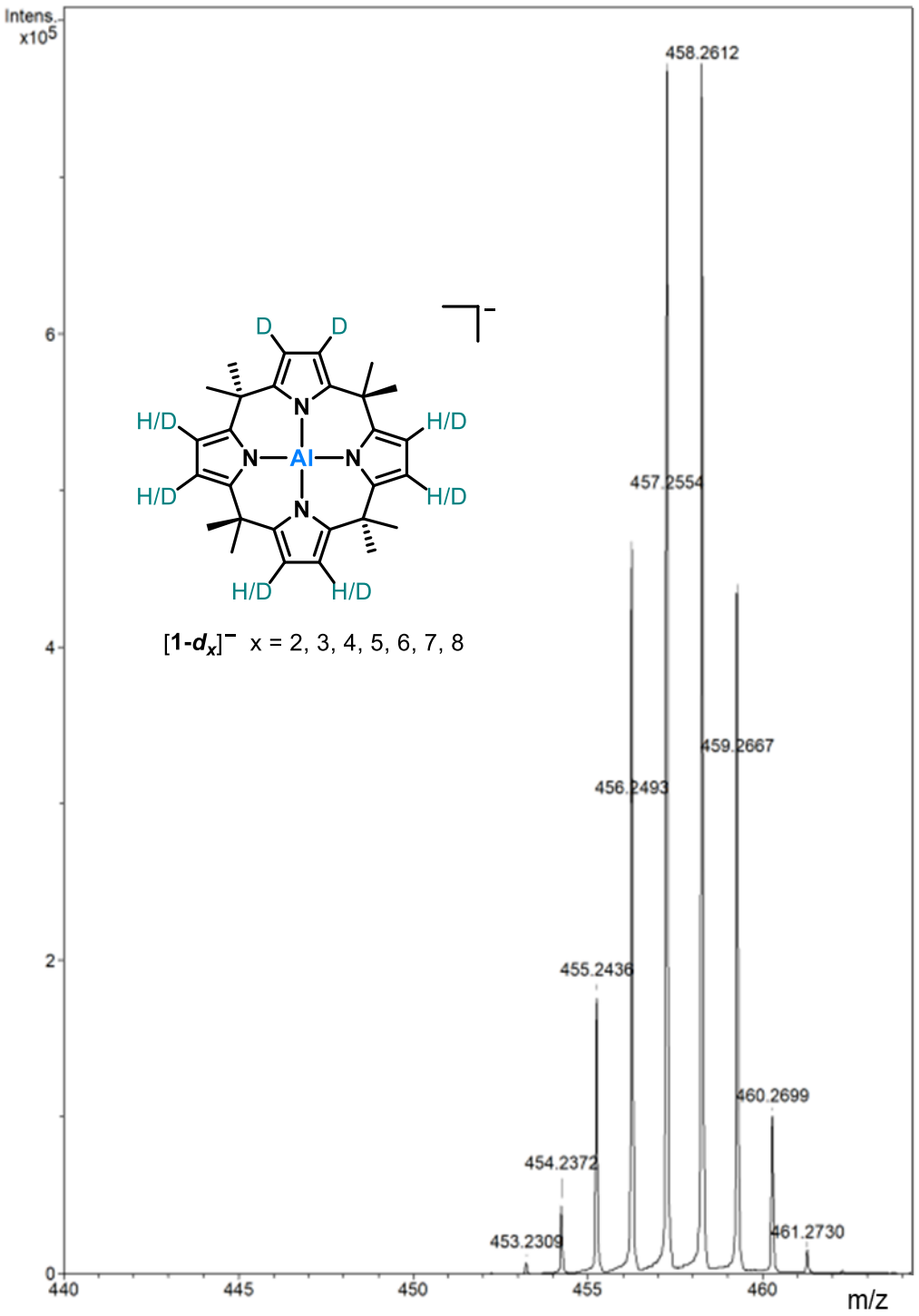


Figure S-11: Excerpt of the mass spectrum of the sample of the H/D exchange experiment after 24 h at room temperature.

The mass spectrum directly shows that the compounds with $C_{28}H_{32}AlN_4$ (m/z = 451.2448) and $C_{28}H_{31}D_1AlN_4$ (m/z = 452.2511) are not present. For all other detected peaks, the relative signal intensities were extracted.

Table S-4: Experimentally determined relative ESI-MS signal intensities of the individual $[\mathbf{1}\text{-}\boldsymbol{d}_x]^-$.

m/z	relative intensity
453.2309	1.00
454.2372	5.86
455.2436	24.00
456.2493	64.14
457.2554	106.00
458.2612	106.00
459.2667	60.29
460.2699	13.86
461.2730	2.14

Within $[\mathbf{1}\text{-}\boldsymbol{d}_x]^-$, the only atoms responsible for a significant isotope pattern are the 28 carbon atoms. The pattern scales with **1.000**, **0.303**, **0.044**, and **0.004**. The scaling factors were obtained with the protpi online MassSpecSimulator (https://www.protpi.ch/Calculator/MassSpecSimulator#MassSpecSimulatorResult, 05.08.2020). So, for each peak the relative contributions (monoisotopic and isotope pattern contribution) using the given scaling factor were calculated:

453.2309: 1.00	– 0 =			1.00
454.2372: 5.86	– **0.303** · 1.00 =			5.5570
455.2436: 24.00	– **0.303** · 5.5570	– **0.044** · 1.00 =		22.2722
456.2493: 64.14	– **0.303** · 22.2722	– **0.044** · 5.557	– **0.004** · 1.00 =	57.1430
257.2554: 106.00	– **0.303** · 57.1430	– **0.044** · 22.2722	– **0.004** · 5.5570 =	87.6835
458.2612: 106.00	– **0.303** · 87.6835	– **0.044** · 57.1430	– **0.004** · 22.2722 =	76.8285
459.2667: 60.29	– **0.303** · 76.8285	– **0.044** · 87.6835	– **0.004** · 57.1430 =	32.9243
460.2699: 13.86	– **0.303** · 32.9243	– **0.044** · 76.8285	– **0.004** · 87.6835 =	0.1527
461.2730: 2.14		– **0.044** · 32.9243	– **0.004** · 76.8285 =	0.3840

The obtained values for m/z = 460.2699 and 461.2730 are close to zero. This is in line with the fact that those two peaks only arise from the isotope pattern of the signals of $[\mathbf{1}\text{-}\boldsymbol{d}_8]^-$ (m/z = 459.2667), $[\mathbf{1}\text{-}\boldsymbol{d}_7]^-$ (m/z = 458.2612, and $[\mathbf{1}\text{-}\boldsymbol{d}_6]^-$ (m/z = 257.2554).

The other numbers represent the relative distribution of the different degrees of deuteration:

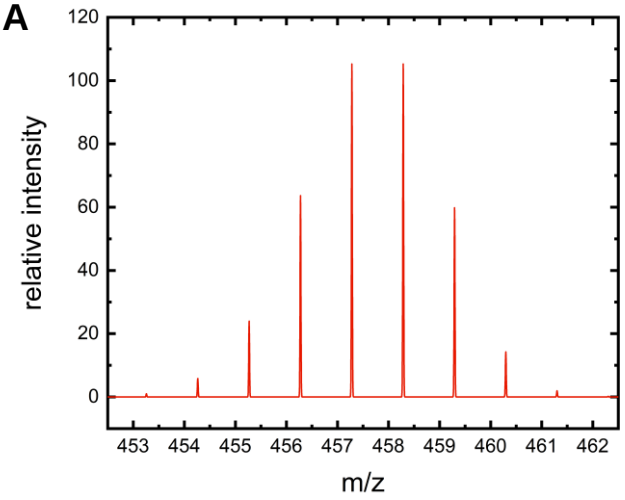
$[\mathbf{1}\text{-}\boldsymbol{d}_0]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_1]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_2]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_3]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_4]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_5]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_6]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_7]^-$	$[\mathbf{1}\text{-}\boldsymbol{d}_8]^-$
0.0	0.0	1.0	5.6	22.3	57.1	87.7	76.8	32.9
0.0%	0.0%	0.4%	2.0%	7.9%	20.2%	30.9%	27.1%	11.6%

The total degree of deuteration is calculated to

$$\frac{0.004 \cdot 2 + 0.02 \cdot 3 + 0.079 \cdot 4 + 0.202 \cdot 5 + 0.309 \cdot 6 + 0.271 \cdot 7 + 0.116 \cdot 8}{8} = \mathbf{76\%}. \qquad \text{(S-15)}$$

To verify the calculated data, the mass spectrum was simulated with the protpi applet (Figure S-12A) and was found in excellent agreement with the experimentally obtained spectrum.

A



B

m/z	relative intensity
453.2564	1.00
454.2636	5.82
455.2691	23.94
456.2745	63.66
457.2818	105.25
458.2872	105.24
459.2927	59.83
460.2964	14.25
461.3000	1.96

Figure S-12: A) Simulated mass spectrum based on the experimentally determined relative amounts of $[\mathbf{1}\text{-}d_x]^-$ given above, and **B)** the extracted relative signal intensities of the simulated spectrum (*c.f.* Table S-4).

S-8. Autoprotolysis

The alcohol addition products show amphoteric behavior manifested in an autoprotolysis equilibrium (Figure S-13, S-22). This equilibrium is sensitive to the solvent environment. It can be enforced by the addition of an excess pentane to the dichloromethane solution of the addition products [PPh4][(RO)-**1***-H]. This was shown for three substrates: ethanol, *para*-methylbenzyl alcohol, and *para*-nitrobenzyl alcohol. The entirety of all observations is discussed in Chapter S-10.

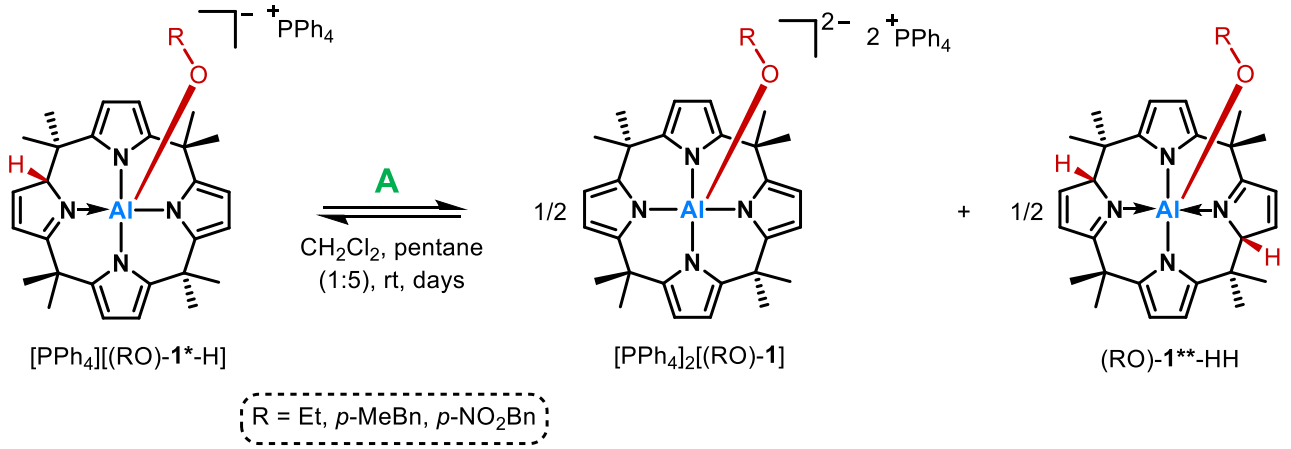
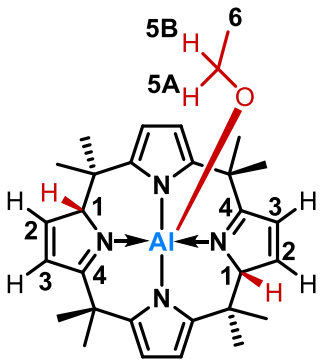


Figure S-13: Autoprotolysis equilibrium of the alcohol addition products [PPh4][(RO)-**1***-H].

General procedure. In a dry nitrogen-filled glove box, [PPh_4][**1**] (45 mg, 56.9 μmol, 1.0 eq) was dissolved in CH_2Cl_2 (1.0 mL) in a crimp-top vial, and the equimolar amount of the alcohol substrate was added in one portion at room temperature. The solution turned yellow (orange in the case of *para*-nitrobenzyl alcohol) upon substrate addition. Pentane (5.0 mL) was added what resulted in the precipitation of a yellow (orange in the case of *para*-nitrobenzyl alcohol) solid. The vial was sealed, and the reaction mixture was allowed to stand for several days (> 2 days) at room temperature. The supernatant was separated from the solid material at the bottom of the vial and was filtered through a PTFE syringe filter. The solvent was removed under reduced pressure to give in all cases, after drying *in vacuo*, pale yellow solids ((RO)-**1****-HH). The orange precipitate (mixture of [PPh_4]$_2$[(RO)-**1**] and [PPh_4][(RO)-**1***-H]) was dried *in vacuo*. Both obtained substances were analyzed by NMR spectroscopy. The $^{13}C\{^1H\}$ NMR signals of the [PPh_4]$_2$[(RO)-**1**] were partially identified by $^1H,^{13}C$ HMBC and $^1H,^{13}C$ HSQC NMR spectroscopy.

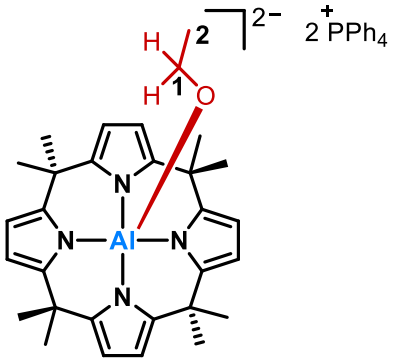
(EtO)-**1****-HH



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.61** (d, $^3J_{HH}$ = 5.3 Hz, 2H, H-2), **7.02** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H-3), **6.04** (d, $^3J_{HH}$ = 3.2 Hz, 2H, β-H), **5.93** (d, $^3J_{HH}$ = 3.2 Hz, 2H, β-H), **4.88** (s, 2H, H-1), **3.39-3.32** (m, 1H, H-5A/5B), **3.11-3.04** (m, 1H, H-5A/5B), **1.84** (s, 6H, α-Me), **1.79** (s, 6H, α-Me), **1.54** (s, 6H, α-Me), **0.86** (t, 3JHH = 7.0 Hz, 3H, H-6), **0.38** (s, 6H, α-Me).

$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **188.9** (C_q, C-4), **155.2** (CH, C-2), **149.6** (C_q, C_q-pyrrole), **143.5** (C_q, C_q-pyrrole), **129.1** (CH, C-3), **104.5** (CH, β-C), **102.5** (CH, β-C), **87.2** (CH, C-1), **56.8** (CH_2, C-5), **39.3** (C_q, α-C), **38.9** (C_q, α-C), **30.7** (CH_3, α-Me), **28.7** (CH_3, α-Me), **27.7** (CH_3, α-Me), **23.3** (CH_3, α-Me), **20.1** (CH_3, C-6).

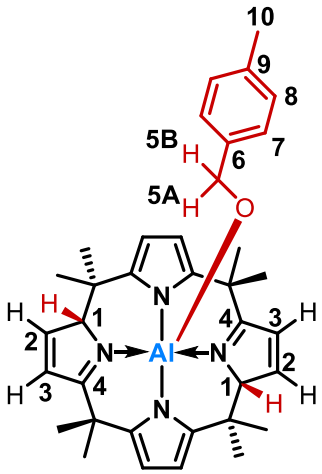
[PPh_4]$_2$[(EtO)-**1**]



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.90-7.82** (m, 8H, PPh_4^+), **7.75-7.66** (m, 16H, PPh_4^+), **7.62-7.53** (m, 16H, PPh_4^+), **5.61** (d, $^3J_{HH}$ = 2.8 Hz, 4H, β-H), **5.54** (d, $^3J_{HH}$ = 2.8 Hz, 4H, β-H), **2.33** (q, $^3J_{HH}$ = 6.8 Hz, 2H, H-1), **0.50** (t, $^3J_{HH}$ = 6.8 Hz, 3H, H-2).

^{13}C{^{1}H} / **^{1}H,^{13}C HSQC** / **^{1}H,^{13}C HMBC NMR** (600 / 151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **148.3** (C_q, C_q-pyrrole), **147.3** (C_q, C_q-pyrrole), **136.1** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+),**117.8** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **99.2** (CH, β-C), **96.8** (CH, β-C), **54.8** (CH_2, C-1), **42.6** (CH_3, α-Me), **36.9** (C_q, α-C), **36.1** (C_q, α-C), **35.6** (CH_3, α-Me), **32.6** (CH_3, α-Me), **26.6** (CH_3, α-Me), **19.6** (CH_3, C-2).

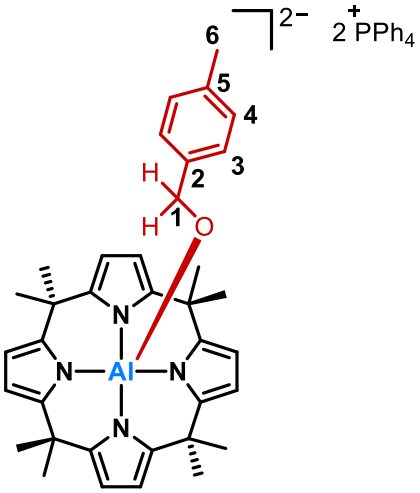
(*p*-MeBnO)-**1****-HH



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.65** (d, $^3J_{HH}$ = 5.3 Hz, 2H, H-2), **7.03** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, H-3), **7.01-6.98** (m, 2H, H-7), **6.96-6.92** (m, 2H, H-8), **6.05** (d, $^3J_{HH}$ = 3.2 Hz, 2H, β-H), **5.96** (d, $^3J_{HH}$ = 3.2 Hz, 2H, β-H), 4.99 (s, 2H, H-1), **4.45** (d, $^3J_{HH}$ = 13.4 Hz, 1H, H-5A/5B), **4.12** (d, $^3J_{HH}$ = 13.4 Hz, 1H, H-5A/5B), **2.22** (s, 3H, H-10), **1.82** (s, 6H, α-Me), **1.69** (s, 6H, α-Me), **1.57** (s, 6H, α-Me), **0.43** (s, 6H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **189.0** (C_q, C-4), **155.3** (CH, C-2), **149.6** (C_q, C_q-pyrrole), **143.6** (C_q, C_q-pyrrole), **142.6** (C_q, C-7), **135.4** (C_q, C-9), **129.0** (CH, C-3), **128.6** (CH, C-8), **126.3** (CH, C-7), **104.6** (CH, β-C), **102.6** (CH, β-C), **87.2** (CH, C-1), **63.4** (CH_2, C-5), **39.3** (C_q, α-C), **38.9** (C_q, α-C), **31.0** (CH_3, α-Me), **28.7** (CH_3, α-Me), **27.7** (CH_3, α-Me), **23.4** (CH_3, α-Me), **21.6** (CH_3, C-10).

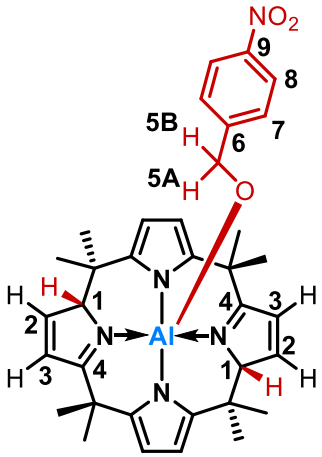
[PPh_4]$_2$[(*p*-MeBnO)-**1**]



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.87-7.79** (m, 8H, PPh_4^+), **7.72-7.63** (m, 16H, PPh_4^+), **7.59-7.50** (m, 16H, PPh_4^+), **6.79-6.76** (m, 2H, H-3), **6.63-6.59** (m, 2H, H-4) **5.59** (d, $^3J_{HH}$ = 2.8 Hz, 4H, β-H), **5.58** (d, $^3J_{HH}$ = 2.8 Hz, 4H, β-H), **3.49** (s, 2H, H-1), **2.06** (s, 3H, H-6), **1.57** (s, 6H, α-Me), **1.52** (s, 6H, α-Me), **1.49** (s, 6H, α-Me), **1.26** (s, 6H, α-Me).

^{13}C{^{1}H} / ^{1}H,^{13}C HSQC / ^{1}H,^{13}C HMBC NMR (600 / 151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **148.2** (C_q, C_q-pyrrole), **147.4** (C_q, C-2), **147.3** (C_q, C_q-pyrrole), **136.1** (CH, d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **132.3** (C_q, C-5), **131.0** (CH, d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **127.5** (CH, C-4), **126.1** (CH, C-3), **117.9** (C_q, d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **99.6** (CH, β-C), **97.1** (CH, β-C), **62.1** (CH_2, C-1), **42.9** (CH_3, α-Me), **36.9** (C_q, α-C), **36.3** (C_q, α-C), **35.7** (CH_3, α-Me), **32.7** (CH_3, α-Me), **26.8** (CH_3, α-Me), **21.0** (CH_3, C-6).

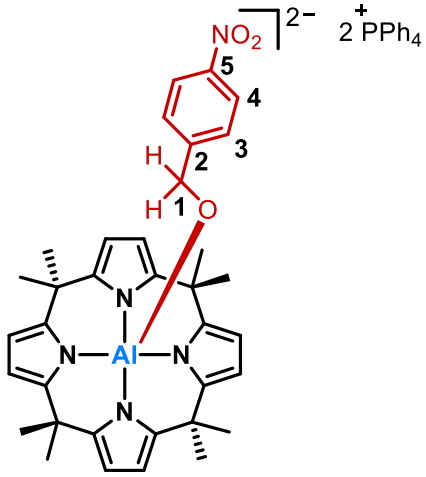
(*p*-NO_2BnO)-**1****-HH



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **8.01-9.97** (m, 2H, H-8), **7.68** (d, $^3J_{HH}$ = 5.3 Hz, 2H, H-2), **7.33-7.30** (m, 2H, H-7), **7.05** (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, H-3), **6.06** (d, $^3J_{HH}$ = 3.2 Hz, 2H, β-H), **5.98** (d, $^3J_{HH}$ = 3.2 Hz, 2H, β-H), **5.03** (s, 2H, H-1), **4.63** (d, $^3J_{HH}$ = 16.1 Hz, 1H, H-5A/5B), **4.28** (d, $^3J_{HH}$ = 16.1 Hz, 1H, H-5A/5B), **1.82** (s, 6H, α-Me), **1.593** (s, 6H, α-Me), **1.590** (s, 6H, α-Me), **0.44** (s, 6H, α-Me).

$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **189.2** (C_q, C-4), **155.5** (CH, C-2), **154.3** (C_q, C-9), **149.6** (C_q, C_q-pyrrole), **146.6** (C_q, C-6), **143.5** (C_q, C_q-pyrrole), **129.1** (CH, C-3), **126.4** (CH, C-7), **123.2** (CH, C-8), **104.8** (CH, β-C), **102.8** (CH, β-C), **87.3** (CH, C-1), **63.0** (CH_2, C-5), **39.4** (C_q, α-C), **38.9** (C_q, α-C), **30.9** (CH_3, α-Me), **28.7** (CH_3, α-Me), **27.7** (CH_3, α-Me), **23.4** (CH_3, α-Me).

[PPh_4]$_2$[(*p*-NO_2BnO)-**1**]



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.87-7.80** (m, 8H, PPh_4^+), **7.71-7.64** (m, 16H, PPh_4^+), **7.62-7.59** (m, 2H, H-3), **7.59-7.51** (m, 16H, PPh_4^+), **7.08-7.04** (m, 2H, H-4) **5.63** (d, $^{3}J_{HH}$ = 2.7 Hz, 4H, β-H), **5.61** (d, $^{3}J_{HH}$ = 2.7 Hz, 4H, β-H), **3.57** (s, 2H, H-1), **1.59** (s, 6H, α-Me), **1.50** (s, 6H, α-Me), **1.47** (s, 6H, α-Me), **1.28** (s, 6H, α-Me).

$^{13}C\{^{1}H\}$ / ^{1}H,^{13}C HSQC / ^{1}H,^{13}C HMBC NMR (600 / 151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **160.5** (C_q, C-2), **148.2** (C_q, C_q-pyrrole), **147.4** (C_q, C_q-pyrrole), **144.9** (C_q, C-5), **136.2** (CH, d, $^{4}J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (CH, d, $^{2}J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (CH, d, $^{3}J_{CP}$ = 12.9 Hz, PPh_4^+), **126.9** (CH, C-4), **122.1** (CH, C-3), **117.8** (C_q, d, $^{1}J_{CP}$ = 89.5 Hz, PPh_4^+), **99.7** (CH, β-C), **97.4** (CH, β-C), **62.7** (CH_2, C-1), **42.8** (CH_3, α-Me), **36.6** (C_q, α-C), **36.2** (C_q, α-C), **35.6** (CH_3, α-Me), **32.8** (CH_3, α-Me), **26.8** (CH_3, α-Me).

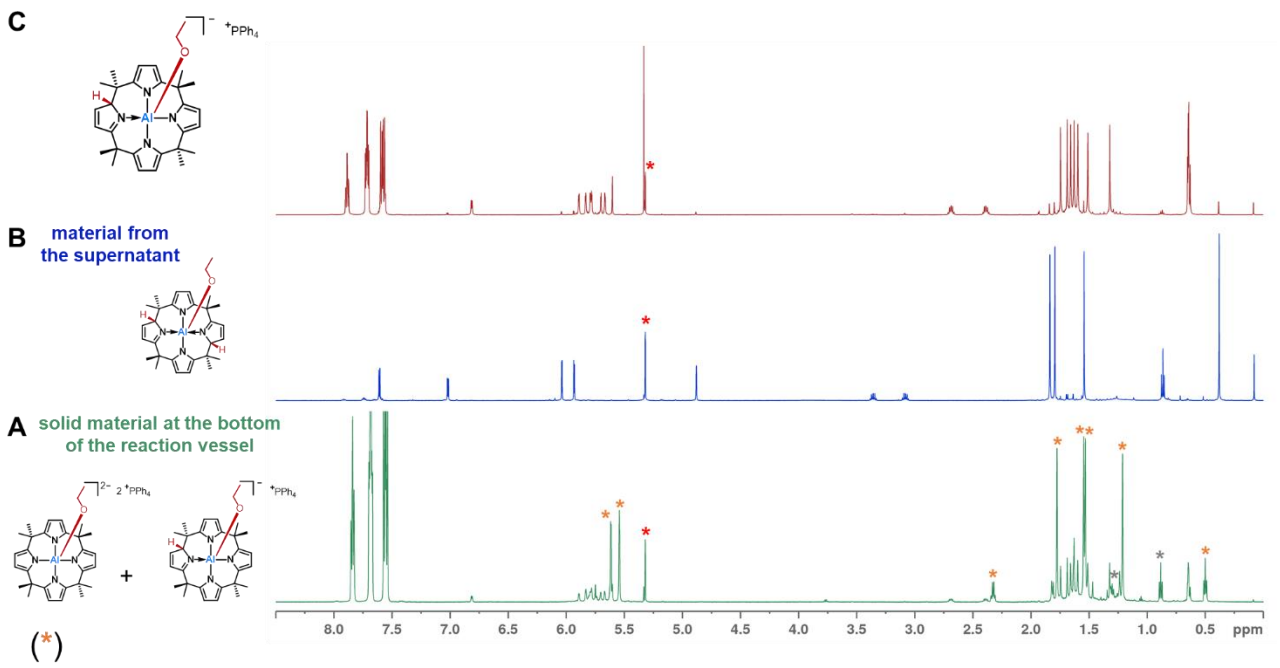


Figure S-14: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K), **A)** of the solid material obtained from the autoprotolysis reaction with ethanol as substrate. It is a mixture of $[PPh_4]_2[(EtO)\text{-}\mathbf{1}]$, $[PPh_4][(EtO)\text{-}\mathbf{1}^*\text{-H}]$ (1:0.5), $[\mathbf{1}]^-$, and EtO^- (1:1) (see Figure S-15). **B)** of the substance, which was dissolved in the supernatant. It is (EtO)-**1****-HH, and **C)** of $[PPh_4][(EtO)\text{-}\mathbf{1}^*\text{-H}]$ for comparison. The signal(s) of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4][\mathbf{1}]$, is marked with a red, those of residual pentane with gray asterisks.

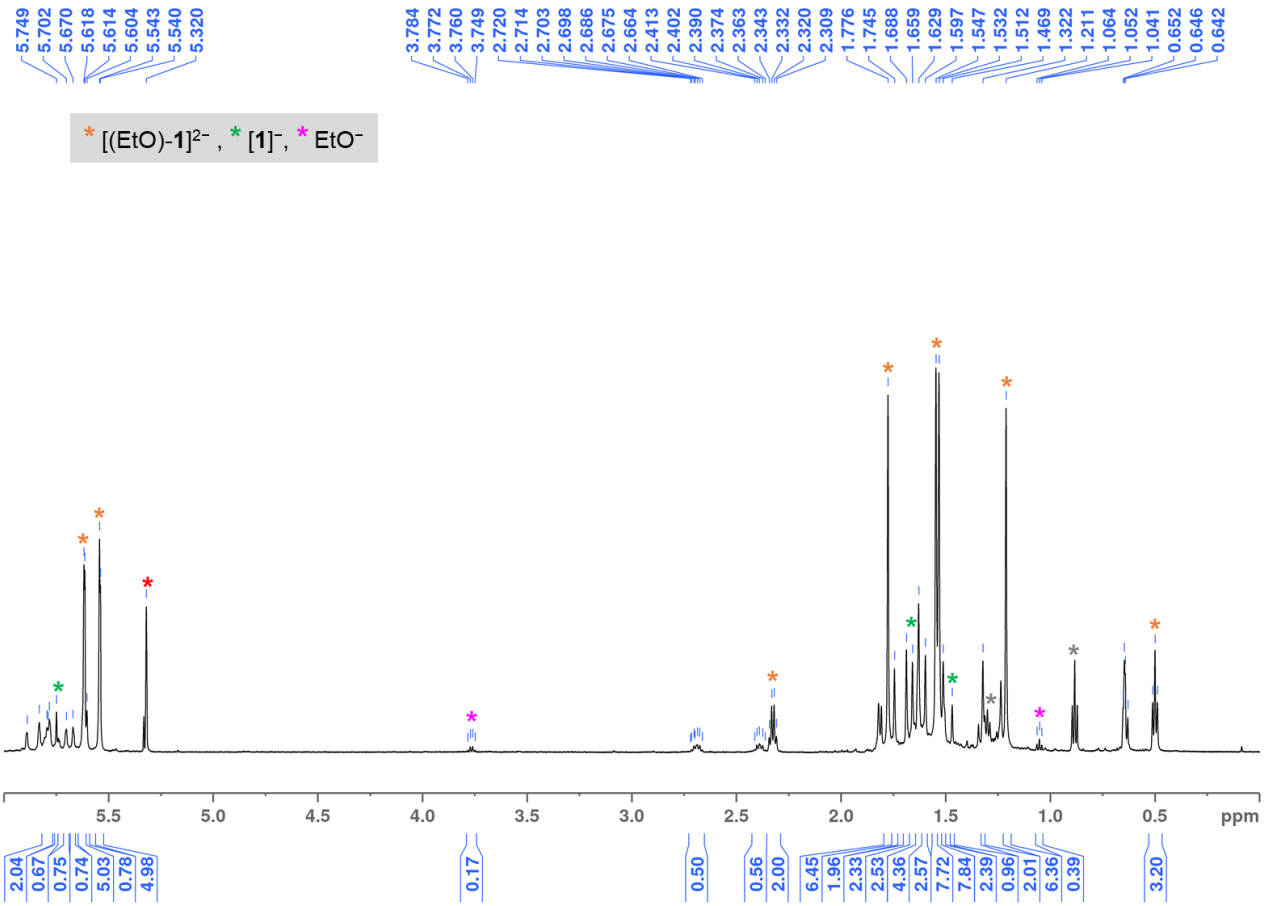


Figure S-15: Excerpt of the ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of the solid material obtained from the autoprotolysis reaction with ethanol as substrate. The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with gray asterisks.

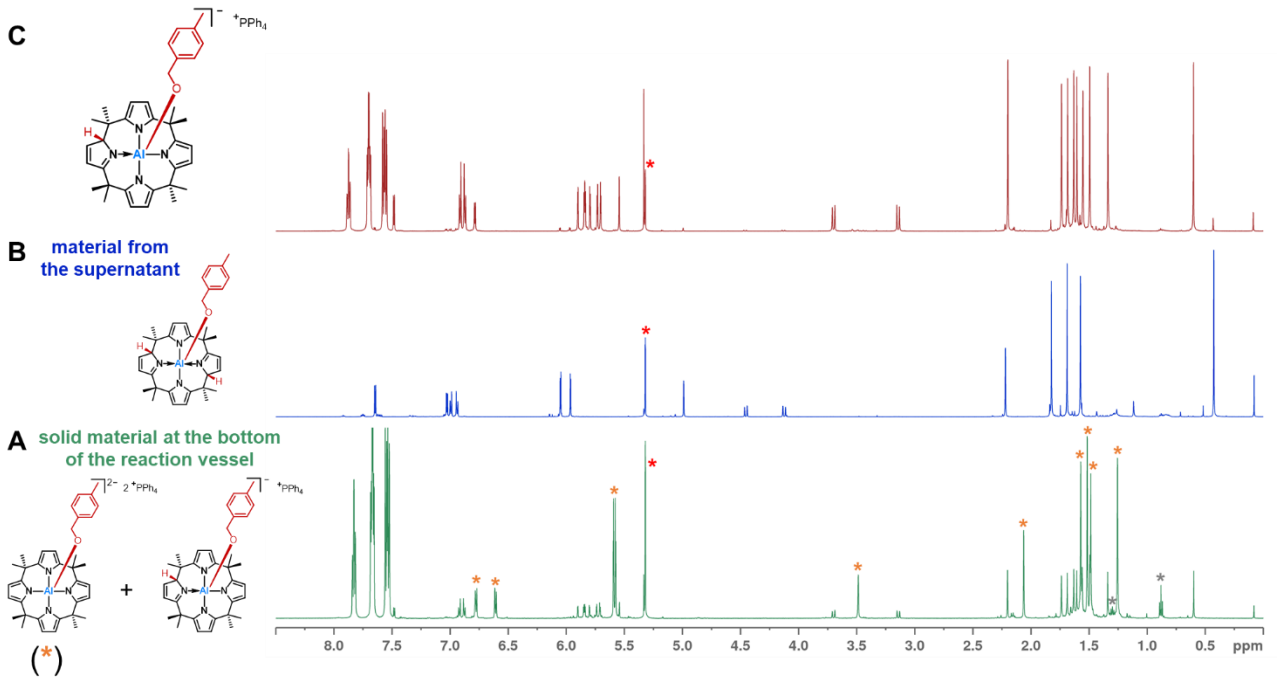


Figure S-16: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K), **A)** of the solid material obtained from the autoprotolysis reaction with *para*-methylbenzyl alcohol. It is a mixture of $[PPh_4]_2$[(*p*-MeBnO)-**1**] and $[PPh_4]$[(*p*-MeBnO)-**1***-H] (1:0.5), **B)** of the substance, which was dissolved in the supernatant. It is (*p*-MeBnO)-**1****-HH, and **C)** of $[PPh_4]$[(*p*-MeBnO)-**1***-H] for comparison. The signal(s) of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4]$[**1**], is marked with a red, those of residual pentane with gray asterisks.

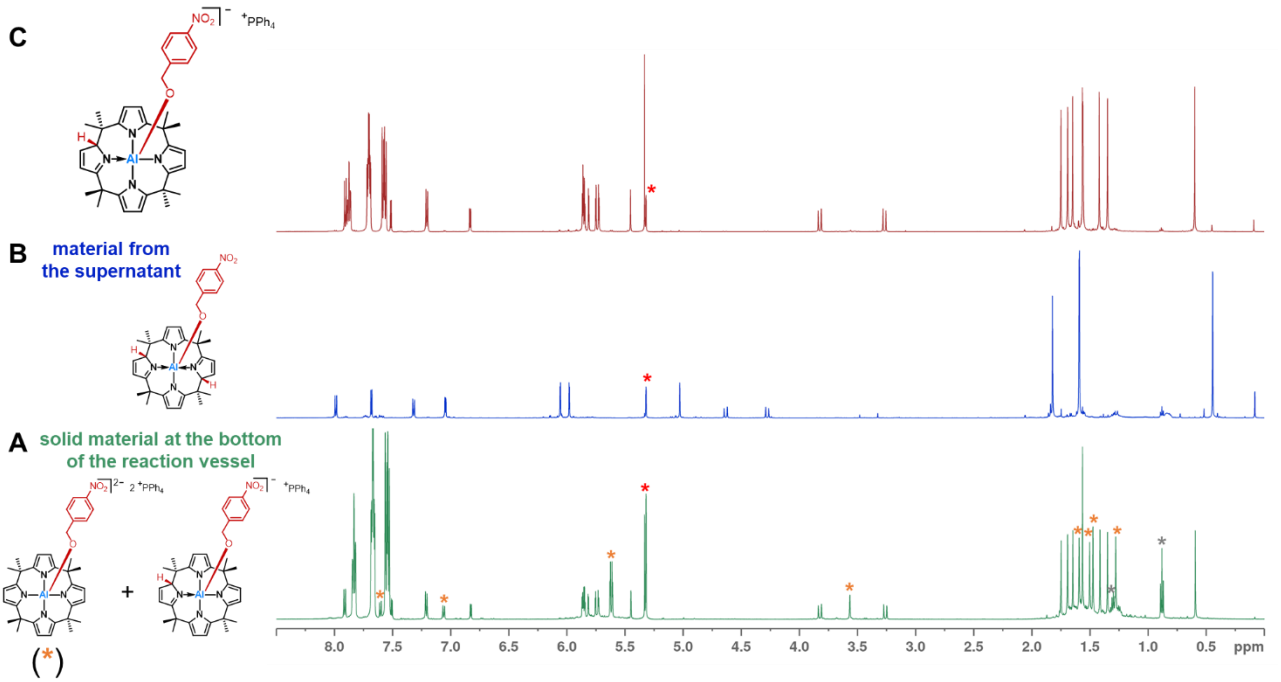


Figure S-17: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K), **A)** of the solid material obtained from the autoprotolysis reaction with *para*-nitrobenzyl alcohol as substrate. It is a mixture of $[PPh_4]_2$[(*p*-NO_2BnO)-**1**] and $[PPh_4]$[(*p*-NO_2BnO)-**1***-H] (1:1.8), **B)** of the substance, which was dissolved in the supernatant. It is (*p*-NO_2BnO)-**1****-HH, and **C)** of $[PPh_4]$[(*p*-NO_2BnO)-**1***-H] for comparison. The signal(s) of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4]$[**1**], is marked with a red, those of residual pentane with gray asterisks.

S-9. Alcohol excess and protonation of [(*p*-BrPhO)-1*-H]$^-$

The behavior of [**1**]$^-$ in the presence of an excess of the alcohol substrates was studied. In general, [**1**]$^-$ can withstand excesses of alcohols and does not undergo alcoholysis (Figure S-18, S-19, S-20). This allowed us to investigate the self-exchange of isopropanol at [**1**]$^-$ (Chapter S-6).

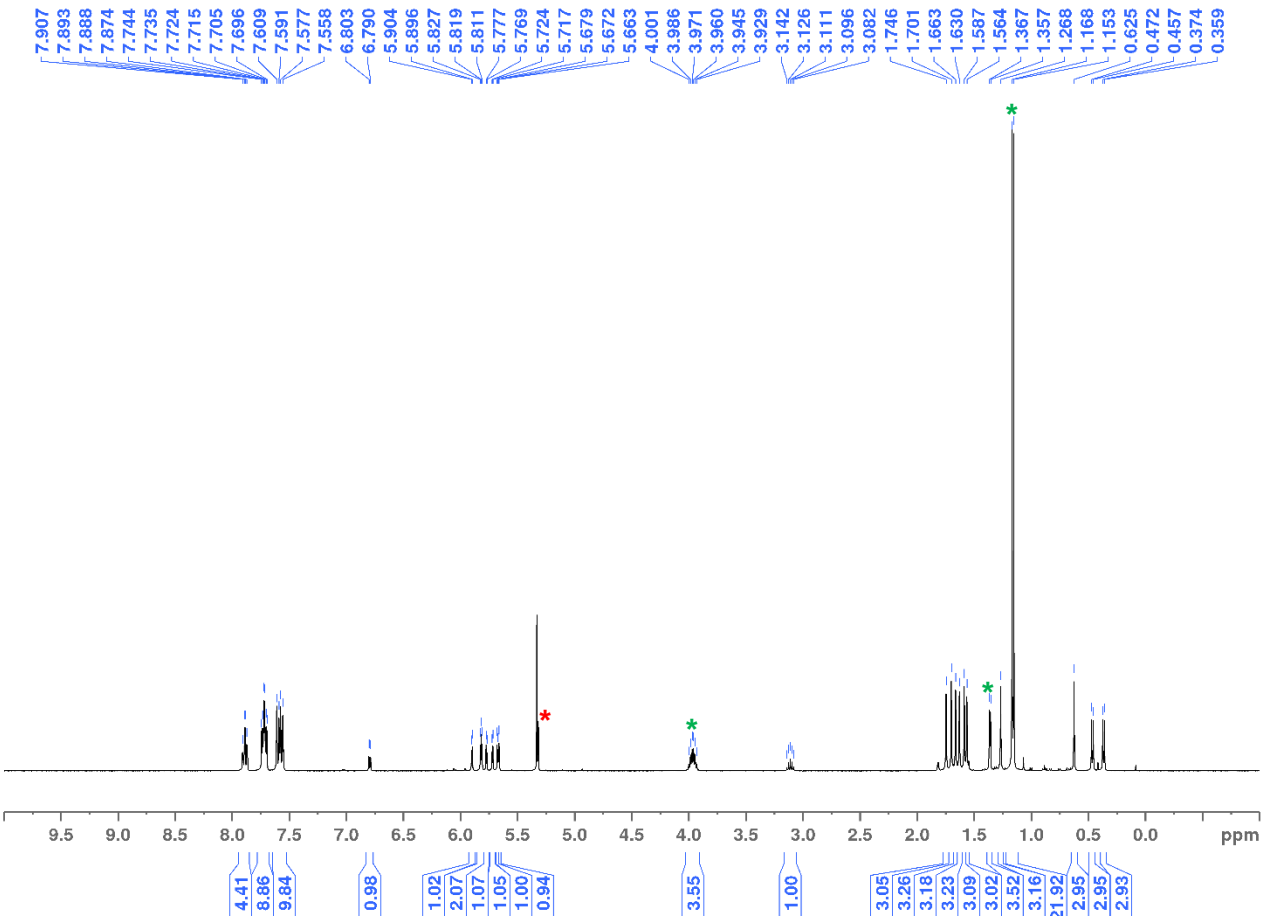


Figure S-18: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [PPh_4][(^{i}PrO)-**1***-H] in the presence of an excess of ^{i}PrOH (*, 3.6 eq). The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

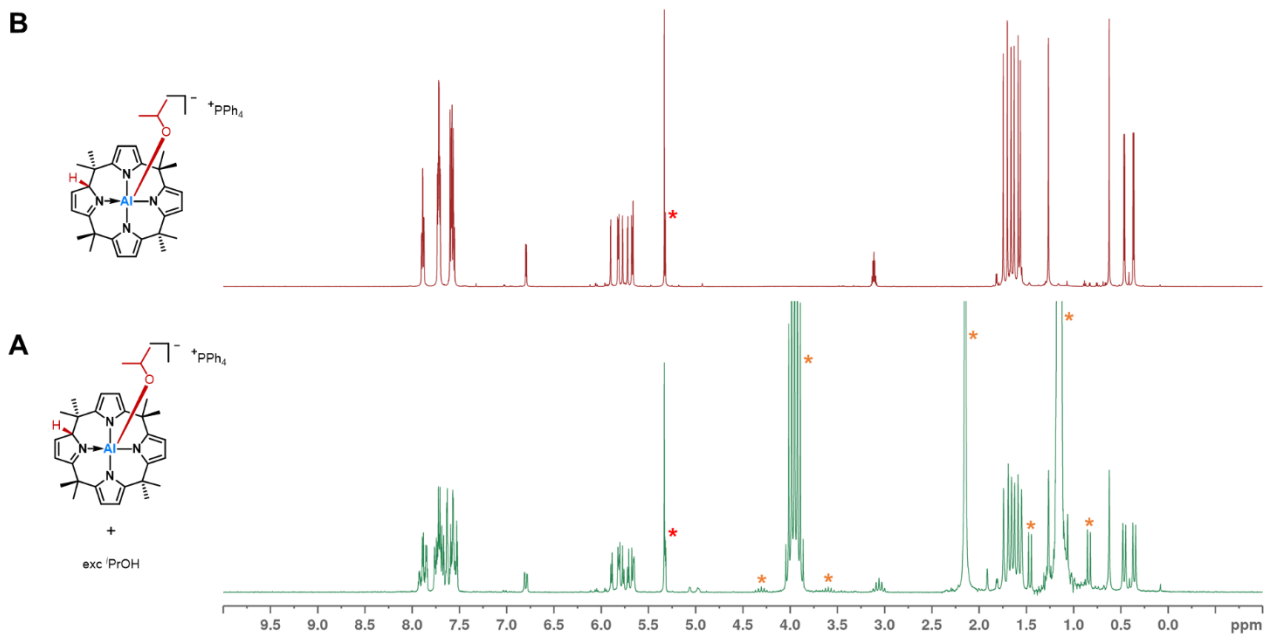


Figure S-19: ^{1}H NMR spectrum (200 MHz (bottom), 600 MHz (top), CD_2Cl_2, 298 K) of **A)** [PPh_4][(^{i}PrOH)-**1***-H] in the presence of an large excess of isopropanol (53 eq relative to the addition product) and of **B)** [PPh_4][(^{i}PrOH)-**1***-H] for comparison. The signals of free isopropanol are marked with orange asterisks. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

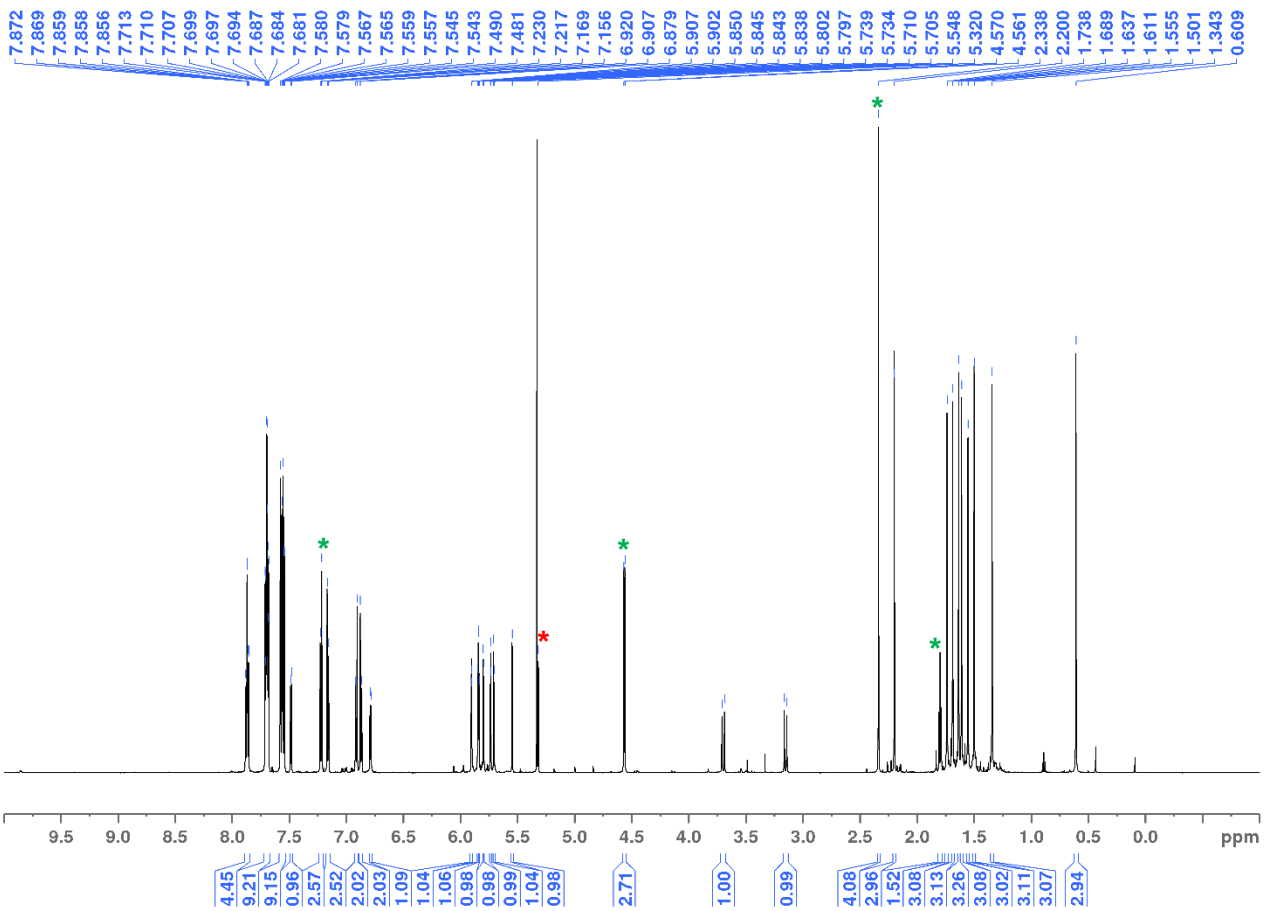


Figure S-20: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-MeBnO)-**1***-H] in the presence of an excess of *p*-MeBnOH (*, 1.4 eq). The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

However, when a significantly more acidic substrate such as *para*-bromophenol was used in excess the quantitative conversion to the neutral (*p*-BrPhO)-**1****-HH was observed by ^{1}H NMR spectroscopy (Figure S-21). This means that a sufficiently acidic OH substrates can quantitatively protonate the alcohol addition products [(*p*-BrPhO)-**1***-H]$^{-}$.

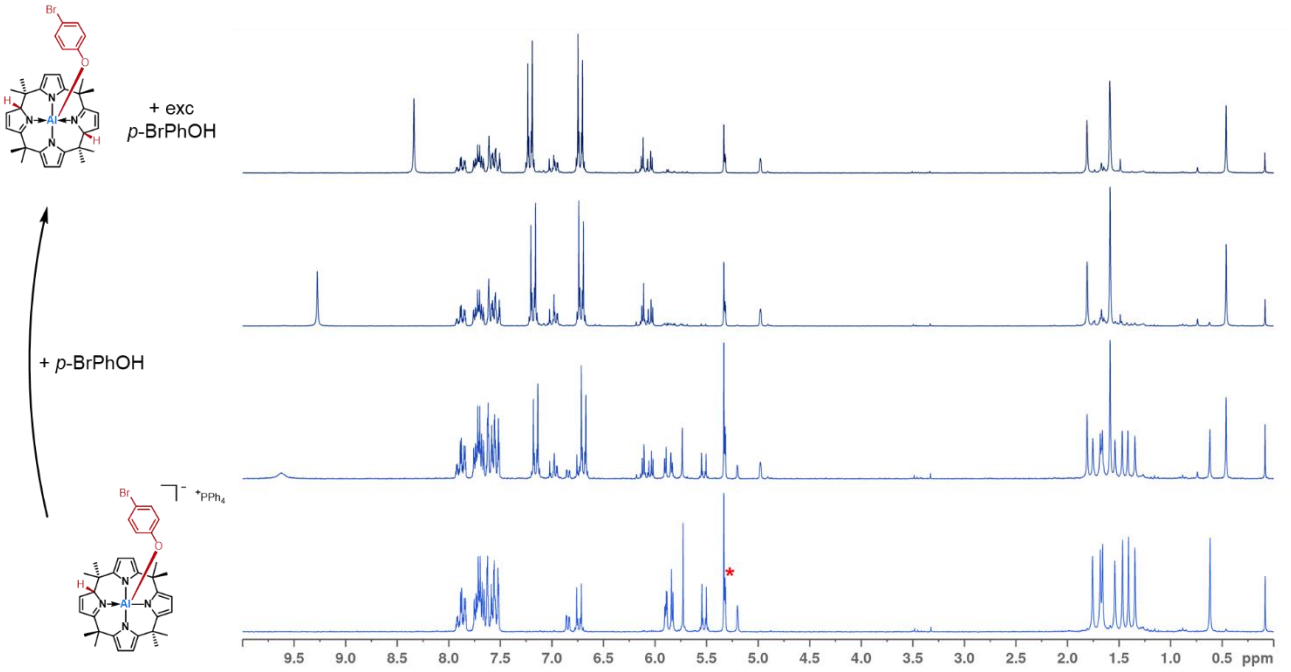


Figure S-21: ^{1}H NMR spectra (200 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-BrPhO)-**1***-H)] (bottom) and after subsequent additions of *p*-BrPhOH portions until full conversion to (*p*-BrPhO)-**1****-HH was achieved (top). The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

S-10. Mechanistic proposals and stereochemical considerations

The ^{1}H NMR signals of the neutral (RO)-**1****-HH species were observed, though only with minute intensities, when the alcohol addition products were prepared (see Chapter S-3). Nonetheless, the ^{1}H NMR signals of the dianionic [(RO)-**1**]$^{2-}$ were never observed, or only in an even weaker intensity compared to the already weak resonances of (RO)-**1****-HH during the alcohol addition reactions. The dianionic species were only isolable through the addition of an excess of pentane to the dichloromethane solutions of [PPh_4][(RO)-**1***-H] (see Chapter S-8). We thus propose the following mechanistic picture (Figure S-22): the equilibrium between the [(RO)-**1***-H]$^{-}$ and [**1**]$^{-}$ + ROH (**B**) provides a small amount of alcohol substrate that does not undergo addition to [**1**]$^{-}$ but instead protonates [(RO)-**1***-H]$^{-}$ to give (RO)-**1****-HH (**C**), as it was detected by ^{1}H NMR spectroscopy. This equilibrium (**C**) also delivers free [**1**]$^{-}$ and the alcoholate RO^{-}. These two species (which are only formed in minute amounts) are now involved in several additional equilibrium reactions such as the normal alcohol addition process to [**1**]$^{-}$ (**B**), most likely fast proton transfer reactions between RO^{-} and ROH, and also the equilibrium between RO^{-} + [**1**]$^{-}$ and [(RO)-**1**]$^{2-}$ (**D**). The equilibrium **D** is strongly lying on the dissociated side, but the dianionic adduct only becomes stable in the solid state. These arguments combined rationalize the fact

that only (RO)-**1****-HH, which is not (to the same extend) part in further fast equilibrium reactions, was observed during the preparation of the alcohol addition products, but not [(RO)-**1**]$^{2-}$.

That the equilibrium **D** is indeed occurring was observed when the solid materials from the autoprotolysis reactions (see Chapter S-8) were analyzed by ^{1}H NMR spectroscopy. Three different substrates were used (EtOH, *p*-MeBnOH, and *p*-NO_2BnOH). First of all, the spectra showed in all cases a mixture of [(RO)-**1**]$^{2-}$ and [(RO)-**1***-H]$^{-}$ (Figure S-14, S-16, S-17). These two species arose from the autoprotolysis equilibrium (**A**). The excess pentane resulted in the crystallization/precipitation of the charged species [(RO)-**1**]$^{2-}$ and [(RO)-**1***-H]$^{-}$ with PPh_4^+ as their counter cations whereas the neutral (RO)-**1****-HH remained dissolved in the supernatant. When now the solid material from the reaction with EtOH was dissolved in dichloromethane-d_2 and was analyzed by ^{1}H NMR spectroscopy, additionally to the signals of [(EtO)-**1**]$^{2-}$ and [(EtO)-**1***-H]$^{-}$ also the characteristic resonances of [**1**]$^{-}$ were found accompanied by a quartet at 3.77 ppm and a triplet at 1.05 ppm which are assigned to the ethanolate anion EtO^{-} (Figure S-15). With *p*-MeBnOH and *p*-NO_2BnOH these observations were not made. Here, no [**1**]$^{-}$ was detected. Thus, with EtOH as substrate, equilibrium **D** delivers all three involved species ([(EtO)-**1**]$^{2-}$, [**1**]$^{-}$, and EtO^{-}) in sufficient concentration for the detection by ^{1}H NMR spectroscopy. With *p*-MeBnOH and *p*-NO_2BnOH, however, equilibrium **D** is strongly lying on the side of [(RO)-**1**]$^{2-}$.

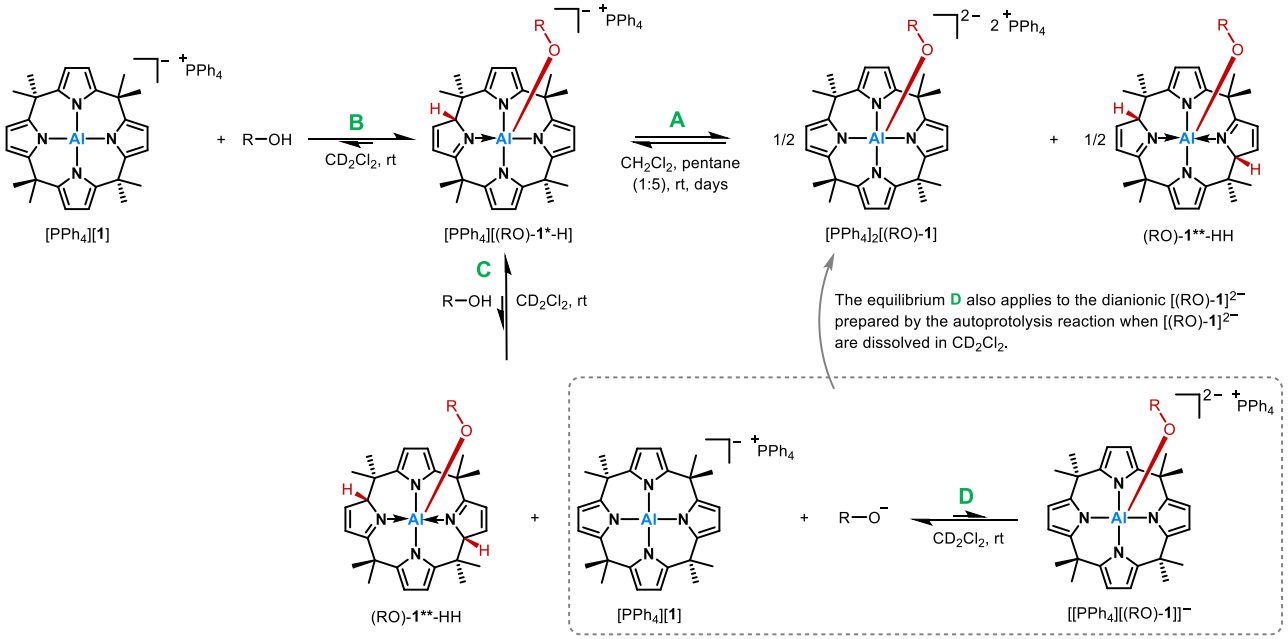


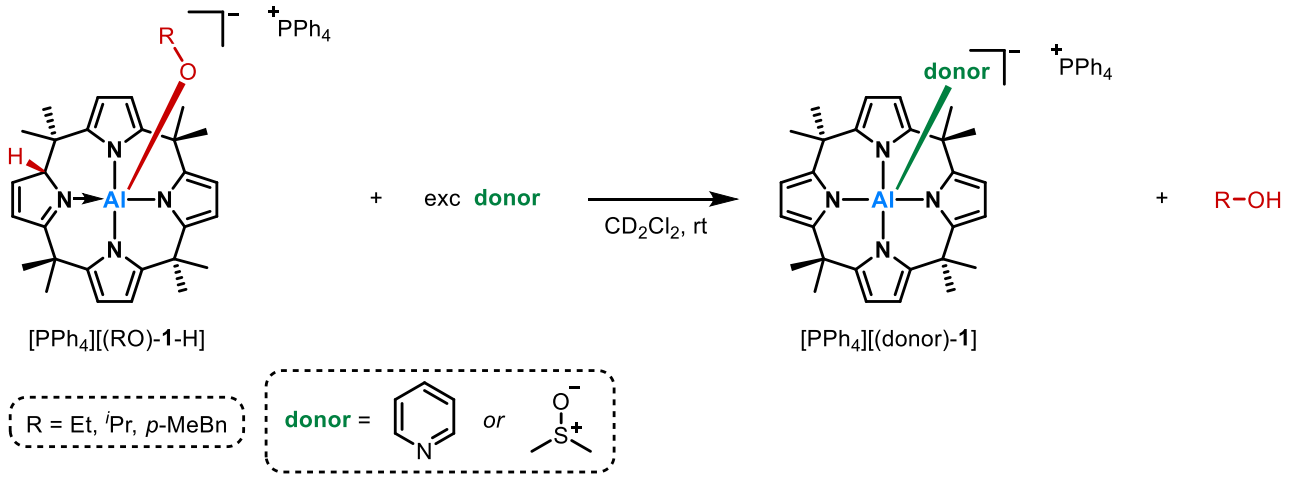
Figure S-22: Mechanistic scenario for the interaction of [**1**]$^{-}$ with protic substrates.

It is also worth to discuss the enrolled mechanistic scenario from a stereochemical point of view. The addition of ROH to [**1**]$^{-}$ produces a stereogenic center in the ligand backbone which is the 2-position of the dearomatized pyrrole ring. In addition, as it was revealed by SCXRD measurements (see Chapter S-12), the alkoxo ligand at the aluminum center and the transferred proton are in a *cis* configuration. No indication of the formation of the respective *trans* diastereomers was found. This supports and is in line with the mechanistic picture of the alcohol addition process, that is coordination of the substrate to the aluminum atom followed by proton transfer to the ligand backbone (see Chapter S-14). Hence, the alcohol addition products [(RO)-**1***-H]$^{-}$ are formed diastereospecifically as a racemic mixture.

Chiral are not only the addition products [(RO)-**1***-H]$^-$, but also the neutral (RO)-**1****-HH. They have two stereogenic centers within two dearomatized pyrrole rings *vis-à-vis* to each other. As shown by SCXRD (see Chapter S-12), both transferred protons and the bound alkoxo ligand are in a *cis* arrangement. Indications of the formation of other regio- and/or stereoisomers was never found. Hence, the neutral (RO)-**1****-HH are formed from the addition product as racemic mixtures in a diastereo- as well as regiospecific manner. The fact that the two transferred protons are in a *cis* orientation with respect to each other rules out the reaction channel in which a second alcohol substrate would coordinate *trans* to the bound alkoxo ligand followed by proton transfer to the backbone. This would result in a *trans* configuration of the two protons in (RO)-**1****-HH. This accords with the quantum chemical calculations (see Chapter S-14). A potential mechanism for the formation of (RO)-**1****-HH might be the dissociation of the alkoxo ligand from the addition products [(RO)-**1***-H]$^-$ and subsequent aluminum-ligand cooperative trapping of a free ROH by the thereby formed **1***-H to give the (RO)-**1****-HH.

S-11. Substitution of alcohol substrates added to [1]$^-$ with donors

The alcohol addition process described in Chapter S-3 can be reversed by Lewis basic donor molecules (pyridine and dimethyl sulfoxide, DMSO). This was shown for four examples (EtOH, ^{i}PrOH, *p*-MeBnOH, *p*-BrPhOH) by treating the alcohol addition products in CD_2Cl_2 (0.6 mL) at room temperature with an excess of pyridine and DMSO, respectively. The substitution reaction was observed by ^{1}H NMR spectroscopy. Quantitative substitution of the strongly binding *p*-BrPhOH was achieved after 90 min at room temperature by dissolving [PPh_4][(*p*-BrPhO)-**1***-H] in DMSO-d_6 (0.6 mL).

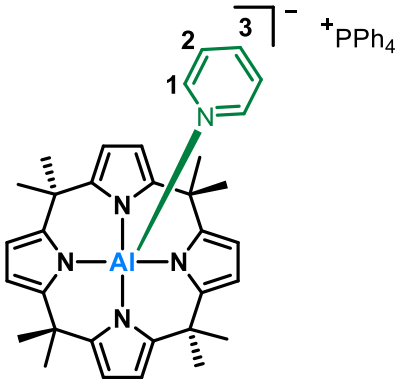


Scheme S-8: Substitution of alcohols added to [**1**]$^-$ with pyridine or DMSO.

To ascertain the identity, the proposed Lewis adducts of pyridine and DMSO with [**1**]$^-$ were prepared separately. For that, in a dry nitrogen-filled glovebox, tetraphenylphosphonium *meso*-octamethylcalix[4]pyrrolato aluminate ([PPh_4][**1**], 10 mg, 12.6 μmol, 1.0 eq) was dissolved in CD_2Cl_2 (0.6 mL) and the equimolar amount of pyridine and DMSO (12.6 μmol, 1.0 eq), respectively, was added to the solution at room temperature. The

reaction mixture turned pale yellow immediately after donor addition. The obtained solutions were analyzed by NMR spectroscopy. In both cases quantitative formation of the Lewis acid/base adduct was observed.

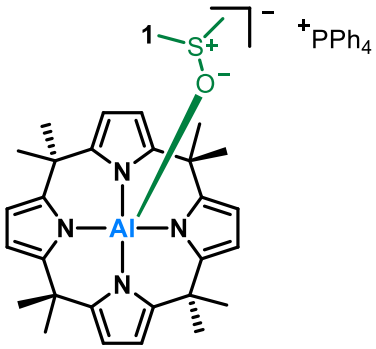
[PPh_4][(pyridine)-**1**]



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.90-7.82** (m, 4H, PPh_4^+), **7.74-7.65** (m, 8H, PPh_4^+), **7.61-7.56** (m, 1H, H-3), **7.60-7.53** (m, 8H, PPh_4^+), **7.12-7.07** (m, 2H, H-2), **6.84-6.81** (m, 2H, H-1), **5.84** (d, $^3J_{HH}$ = 2.9 Hz, 4H, β-H), **5.74** (d, $^3J_{HH}$ = 2.9 Hz, 4H, β-H), **1.70** (s, 6H, α-Me), **1.47** (s, 6H, α-Me), **1.46** (s, 6H, α-Me), **0.05** (s, 6H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **149.5** (CH, C-1), **148.6** (C_q, C_q-pyrrole), **148.1** (C_q, C_q-pyrrole), **140.2** (CH, C-3), **136.2** (d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **125.3** (CH, C-2), **117.8** (d, $^1J_{CP}$ = 89.6 Hz, PPh_4^+), **102.1** (CH, β-C), **99.7** (CH, β-C), **40.8** (CH_3, α-Me), **36.3** (CH_3, α-Me), **36.1** (C_q, α-C), **35.9** (C_q, α-C), **34.5** (CH_3, α-Me), **26.4** (CH_3, α-Me).

[PPh_4][(dmso)-**1**]



^{1}H NMR (600 MHz, CD_2Cl_2, 295 K), δ [ppm] = **7.87-7.81** (m, 4H, PPh_4^+), **7.70-7.64** (m, 8H, PPh_4^+), **7.58-7.51** (m, 8H, PPh_4^+), **5.83** (d, $^3J_{HH}$ = 2.9 Hz, 4H, β-H), **5.76** (d, $^3J_{HH}$ = 2.9 Hz, 4H, β-H), **2.05** (s, 6H, H-1), **1.66** (s, 6H, α-Me), **1.65** (s, 6H, α-Me), **1.29** (s, 6H, α-Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 295 K), δ [ppm] = **147.9** (C_q, C_q-pyrrole), **146.9** (C_q, C_q-pyrrole), **136.2** (d, $^4J_{CP}$ = 3.0 Hz, PPh_4^+), **134.8** (d, $^2J_{CP}$ = 10.3 Hz, PPh_4^+), **131.0** (d, $^3J_{CP}$ = 12.9 Hz, PPh_4^+), **117.8** (d, $^1J_{CP}$ = 89.6 Hz,

PPh_4^+), **101.8** (CH, β-C), **99.8** (CH, β-C), **41.7** (CH_3, α-Me), **38.4** (CH_3, α-Me), **36.4** (C_q, a-C), **35.9** (C_q, a-C), **34.5** (CH_3, C-1), **33.5** (CH_3, α-Me), **26.3** (CH_3, α-Me).

EtOH substitution

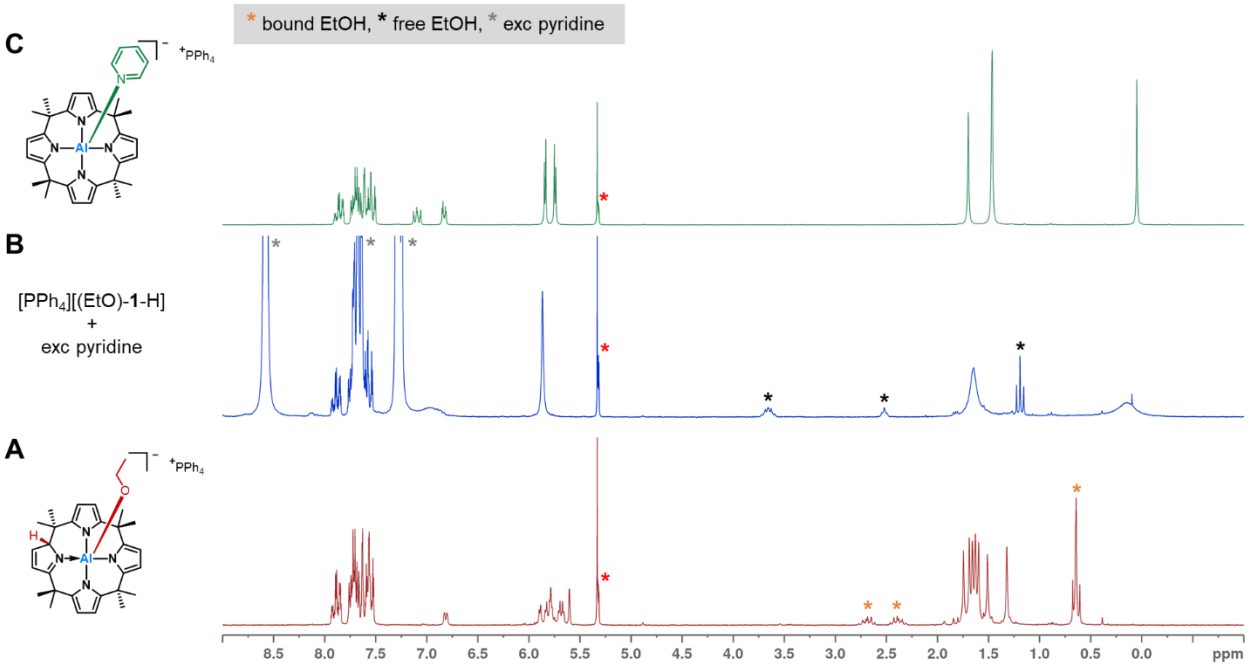


Figure S-23: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K), of **A)** [PPh4][(EtO)-**1***-H], **B)** [PPh4][(EtO)-**1***-H] with an added excess of pyridine, and **C)** of [PPh4][(pyridine)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

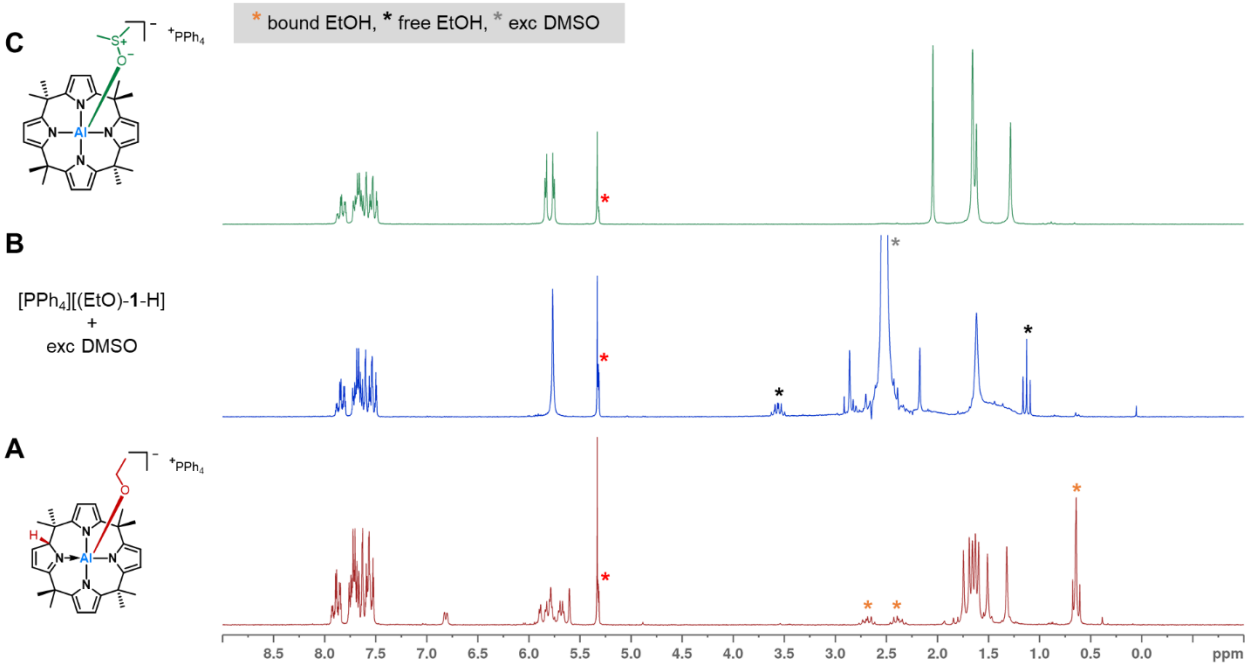


Figure S-24: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K), of **A)** [PPh4][(EtO)-**1***-H], **B)** [PPh4][(EtO)-**1***-H] with an added excess of dimethyl sulfoxide, and **C)** of [PPh4][(dmso)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

^{i}PrOH substitution

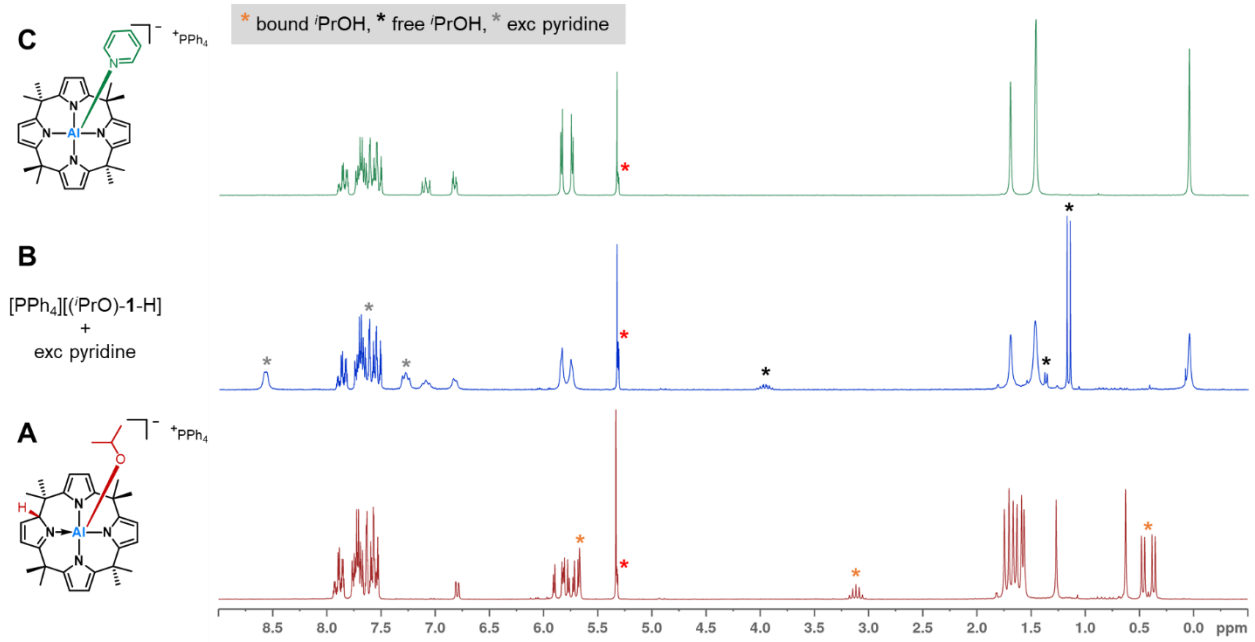


Figure S-25: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K), of **A)** [PPh4][(^{i}PrO)-**1***-H], **B)** [PPh4][(^{i}PrO)-**1***-H] with an added excess of pyridine, and **C)** of [PPh4][(pyridine)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

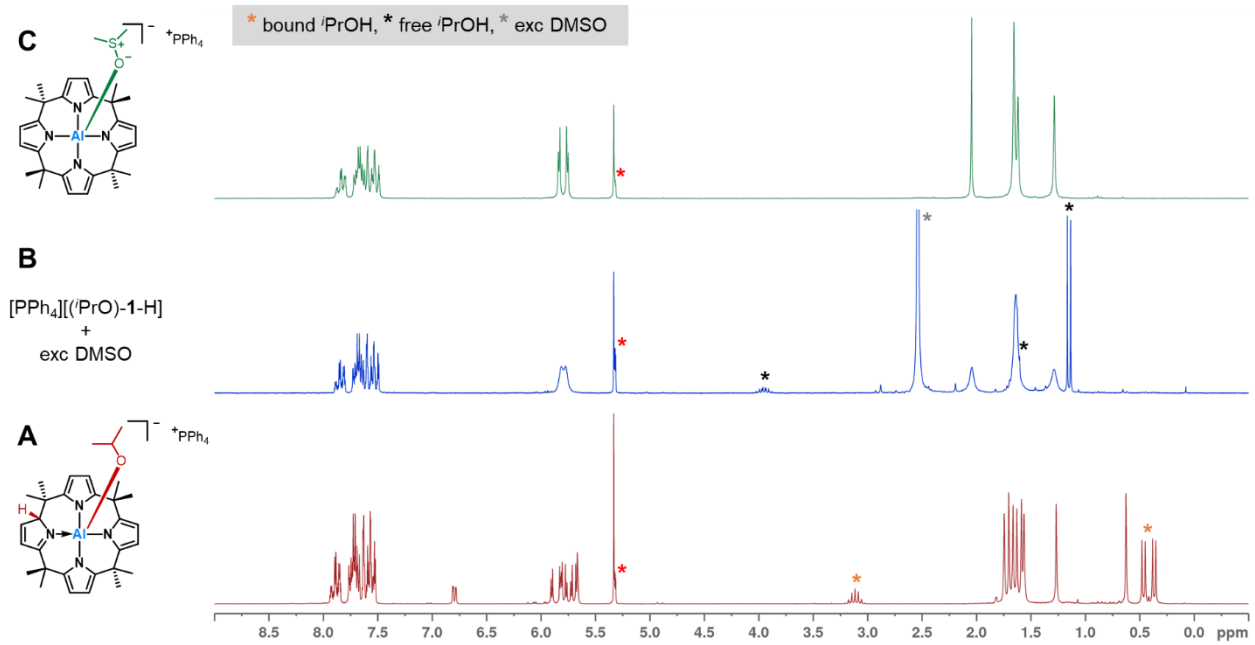


Figure S-26: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K), of **A)** [PPh4][(^{i}PrO)-**1***-H], **B)** [PPh4][(^{i}PrO)-**1***-H] with an added excess of dimethyl sulfoxide, and **C)** of [PPh4][(dmso)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

***p*-MeBnOH substitution**

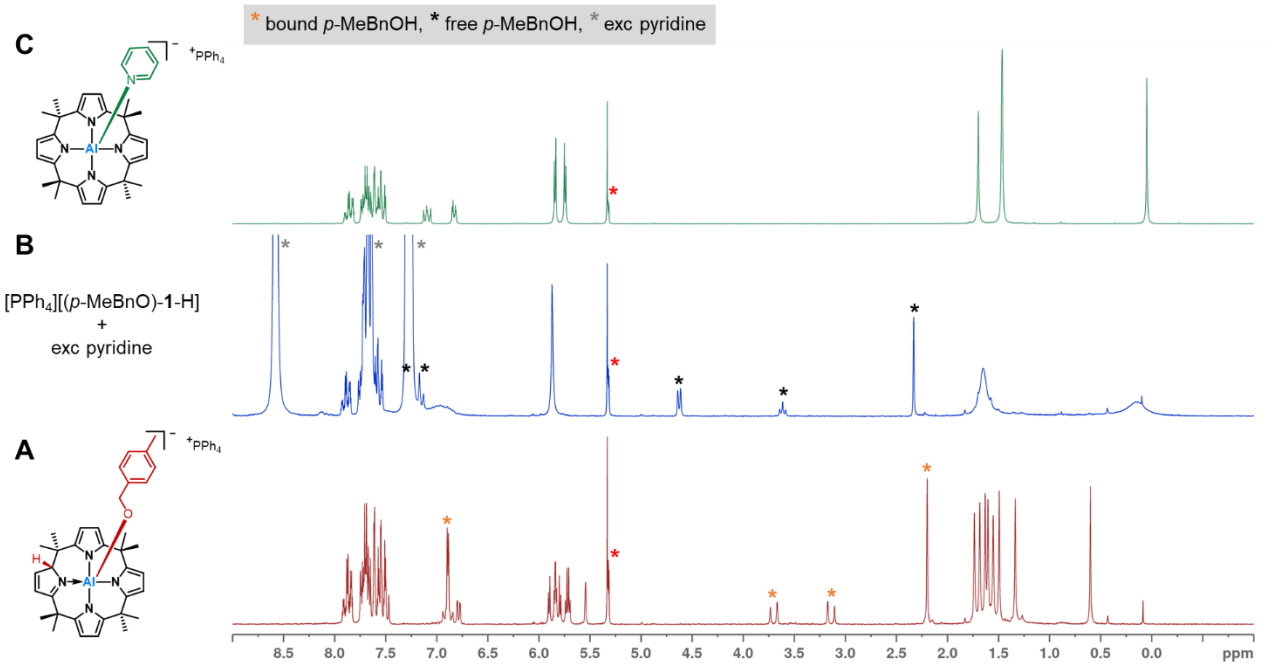


Figure S-27: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K), of **A)** [PPh4][(*p*-MeBnO)-**1***-H], **B)** [PPh4][(*p*-MeBnO)-**1***-H] with an added excess of pyridine, and **C)** of [PPh4][(pyridine)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

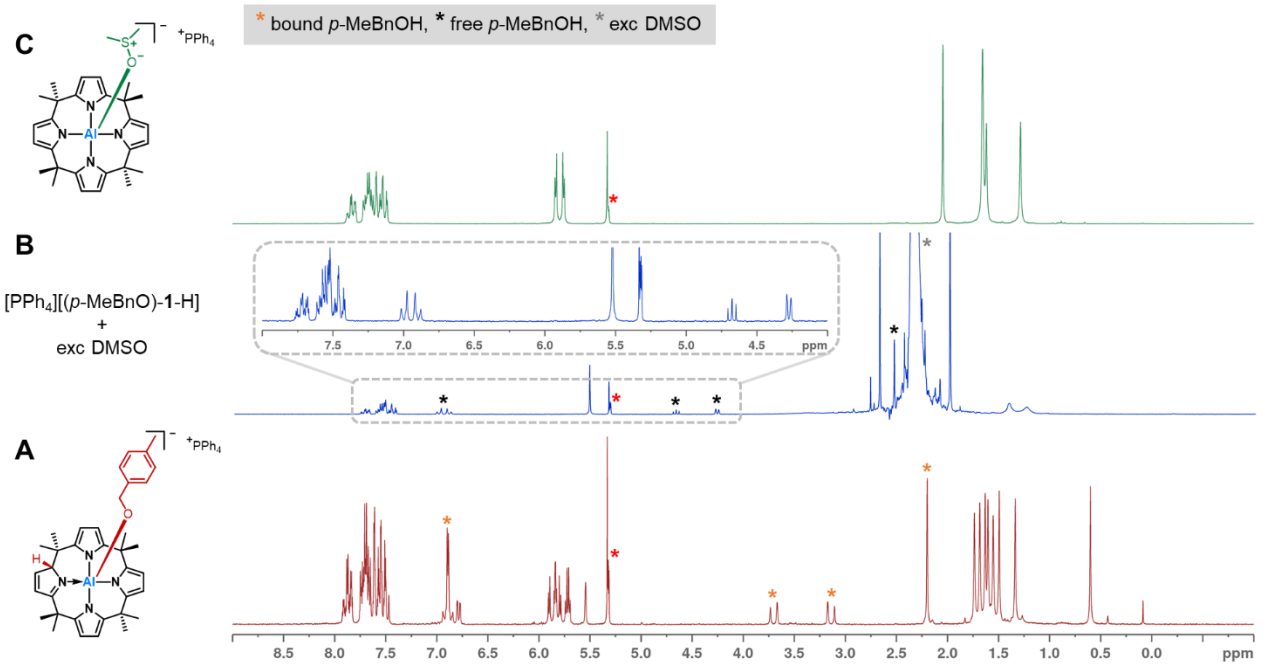


Figure S-28: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K), of **A)** [PPh4][(*p*-MeBnO)-**1***-H], **B)** [PPh4][(*p*-MeBnO)-**1***-H] with an added excess of dimethyl sulfoxide, and **C)** of [PPh4][(dmso)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

***p*-BrPhOH substitution**

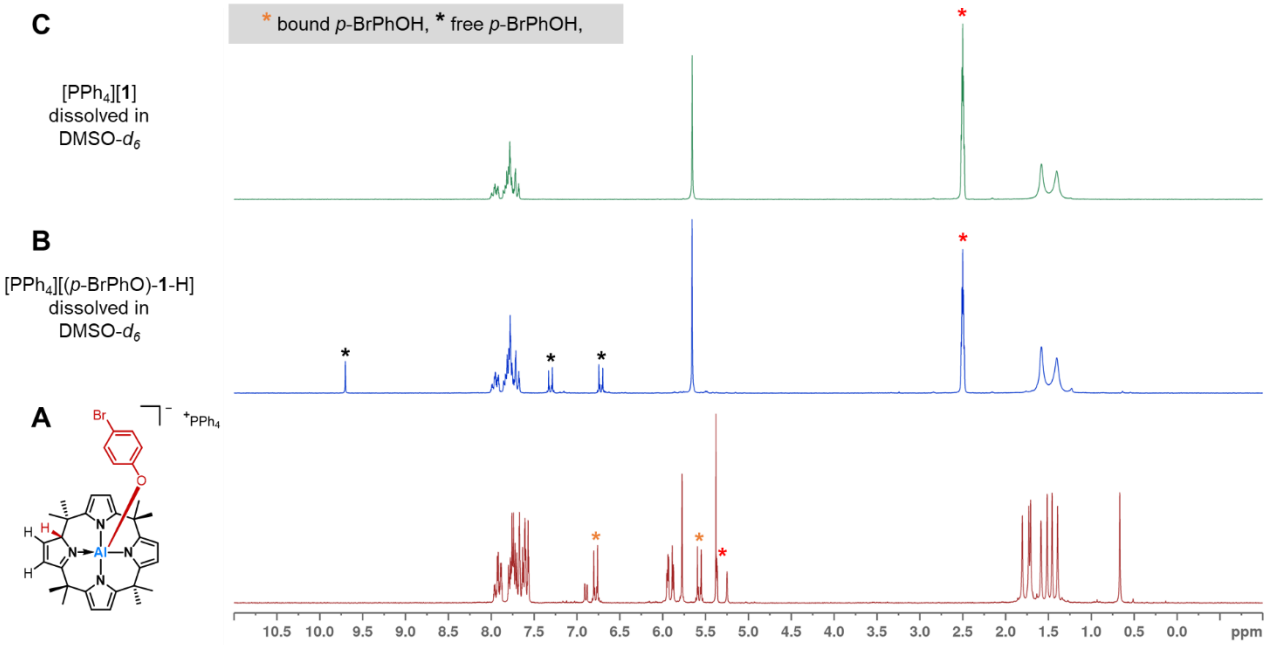


Figure S-29: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2 (**A**), DMSO-d_6 (**B**, **C**), 298 K), of **A)** [PPh4][(*p*-BrPhO)-**1***-H], **B)** [PPh4][(*p*-BrPhO)-**1***-H] dissolved in DMSO-d_6, and **C)** of [PPh4][**1**] dissolved in DMSO-d_6. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

S-12. X ray crystallography

Crystals were grown using the following conditions: [PPh_4][(*p*-BrPhO)-**1***-H]: CH_2Cl_2/toluene solution at -40 °C, (EtO)-**1****-HH and [PPh_4]$_2$[(EtO)-**1**]: [PPh_4][(EtO)-**1***-H] was prepared in CH_2Cl_2 and five volume equivalents of pentane were added (see Chapter S-8). This mixture produced both crystalline materials at room temperature. [PPh_4][(EtO)-**1***-H]: CH_2Cl_2/diethyl ether at -40 °C.

For SCXRD measurements, a suitable crystal was picked from the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a cryo loop. A Bruker APEX-III CCD diffractometer with a low-temperature unit using Mo-Kα radiation, chromated by mirror optics, was used for f and ω scans. Data acquisition was done at 100.0 K. A strategy for data collection was calculated with Bruker's APEX3 software. The same program was used for processing of collected data. Data reduction, scaling, and absorption corrections were done with SAINT. SA-DABS-2016/2 was used for multi-scan absorption correction. Structures were solved with dual methods as implemented in the ShelXT 2014/5 structure solution program. Structure refinement was carried out by full matrix least squares minimization on F^2 using the 2018/3 version of ShelXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model. Handling of the structural data during solution and refinement was performed with the Olex2 v1.3 graphical interface.[10]

Data visualization was achieved with Mercury 4.1.3.[11-13] All thermal displacement ellipsoids are shown at the 50% probability level.

[PPh_4][(*p*-BrPhO)-**1***-H]

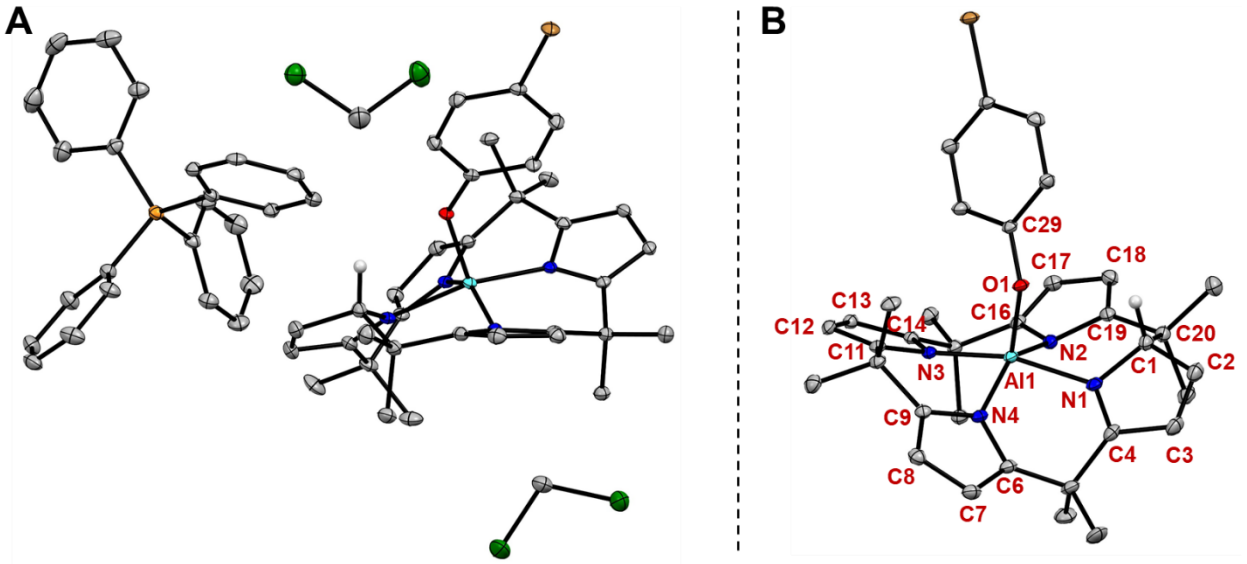


Figure S-30: A) Asymmetric unit of the crystal lattice found for [PPh_4][(*p*-BrPhO)-**1***-H], and **B)** molecular structure of the respective anion, [(*p*-BrPhO)-**1***-H]$^-$. All hydrogen atoms except for the one which was transferred to the ligand backbone are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.
Selected bond lengths [pm]: **Al1-N1:** 202.1(3), **Al1-N2:** 194.3(3), **Al1-N3:** 193.0(2), **Al1-N4:** 194.9(2), **Al1-O1:** 179.1(2),**O1-C29:** 134.3(3), **N1-C1:** 145.7(4), **C1-C2:** 149.4(4), **C3-C2:** 132.6(5), **C3-C4:** 146.4(4), **N1-C4:** 130.0(4), **N2-C16:** 139.4(4), **C16-C17:** 137.0(4), **C17-C18:** 141.5(4), **C19-C18:** 136.6(4), **N2-C19:** 139.7(4), **N3-C11:** 139.5(4), **C11-C12:** 138.0(4), **C13-C12:** 141.7(4), **C13-C14:** 137.5(4), **N3-C14:** 137.7(4), **N4-C6:** 139.1(4), **C6-C7:** 136.9(4), **C7-C8:** 141.9(4), **C9-C8:** 137.7(4), **N4-C9:** 138.4(4).
Selected bond angles [°]: **N3-Al1-N1:** 165.33(10), **N2-Al1-N4:** 147.90(10), **O1-Al1-N3:** 104.23(10), **O1-Al1-N2:** 102.80(10), **O1-Al1-N4:** 107.97(10), **O1-Al1-N1:** 90.05(9), **N1-C1-C20:** 108.9(2), **N1-C1-C2:** 104.1(2), **C2-C1-C20:** 114.1(2), **C29-O1-Al1:** 134.23(17).

Table S-5: Crystal data and structure refinement for [PPh_4][(*p*-BrPhO)-**1***-H] (mo_lms44b_ii_0ma).

Identification code	mo_lms44b_ii_0ma
Empirical formula	$C_{60}H_{61}AlBrCl_4N_4OP$
Formula weight	1133.78
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.7658(18)
b/Å	27.696(6)
c/Å	20.719(4)
α/°	90
β/°	102.380(7)
γ/°	90
Volume/Å^3	5473.6(19)
Z	4
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	1.037
F(000)	2352.0
Crystal size/mm^3	0.258 × 0.246 × 0.132
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.026 to 51
Index ranges	-11 ≤ h ≤ 11, -33 ≤ k ≤ 33, -25 ≤ l ≤ 25
Reflections collected	227575
Independent reflections	10164 [R_{int} = 0.0993, R_{sigma} = 0.0261]
Data/restraints/parameters	10164/0/657

Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0472, wR_2 = 0.1251
Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.1338
Largest diff. peak/hole / e $Å^{-3}$	0.99/-0.84

(EtO)-**1****-HH

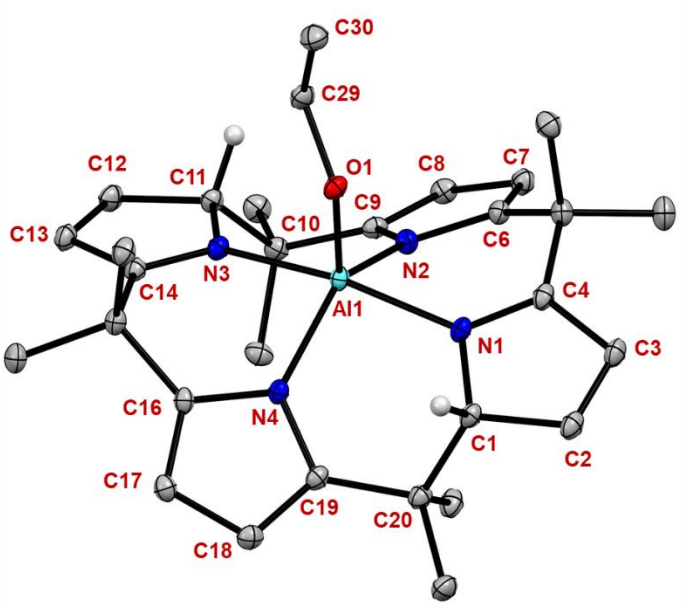


Figure S-31: Asymmetric unit of the crystal lattice found for (EtO)-**1****-HH. All hydrogen atoms except for the two which were transferred to the ligand backbone are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.
Selected bond lengths [pm]: **Al1-O1:** 175.31(18), **Al1-N1:** 202.68(19), **Al1-N2:** 192.0(2), **Al1-N3:** 204.14(19), **Al1-N4:** 194.2(2), **N1-C1:** 147.5(3), **C1-C2:** 148.6(3), **C2-C3:** 133.7(4), **C3-C4:** 146.4(3), **N1-C4:** 130.0(3), **N2-C6:** 139.7(3), **C6-C7:** 136.8(3), **C7-C8:** 141.5(3), **C8-C9:** 137.1(3), **N2-C9:** 139.7(3), **N3-C11:** 147.1(3), **C11-C12:** 148.6(3), **C12-C13:** 132.8(4), **C13-C14:** 146.7(3), **N3-C14:** 129.4(3), **N4-C16:** 139.6(3), **C16-C17:** 137.0(3), **C17-C18:** 141.4(3), **C18-C19:** 136.9(3), **N4-C19:** 139.7(3), **O1-C29:** 141.1(3), **C29-C30:** 151.1(4).
Selected bond angles [°]: **N1-Al1-N3:** 169.31(9), **N2-Al1-N4:** 135.06(9), **N1-C1-C2:** 104.4(2), **N1-C1-C20:** 109.93(18), **C2-C1-C20:** 117.4(2), **N3-C11-C10:** 110.10(18), **N3-C11-C12:** 103.96(19), **C12-C11-C10:** 118.00(19), **C29-O1-Al1:** 126.25(15), **O1-Al1-N1:** 93.91(8), **O1-Al1-N2:** 110.69(9), **O1-Al1-N3:** 96.76(8), **O1-Al1-N4:** 114.23(9).

Table S-6: Crystal data and structure refinement for (EtO)-**1****-HH (mo_lms045_neu_0ba).

Identification code	mo_lms045_neu_0ba
Empirical formula	$C_{30}H_{39}AlN_4O$
Formula weight	498.63
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	9.7760(9)
b/Å	25.127(2)
c/Å	11.0644(10)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2717.9(4)
Z	4
$\rho_{calc}g/cm^3$	1.219
μ/mm^{-1}	0.104
F(000)	1072.0

Crystal size/mm^3	0.454 × 0.173 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.47 to 56.652
Index ranges	-13 ≤ h ≤ 13, -33 ≤ k ≤ 33, -14 ≤ l ≤ 14
Reflections collected	61625
Independent reflections	6756 [R_{int} = 0.0718, R_{sigma} = 0.0365]
Data/restraints/parameters	6756/1/334
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0792
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.0852
Largest diff. peak/hole / e Å^{-3}	0.22/-0.24
Flack parameter	-0.02(7)

[PPh_4][(EtO)-**1***-H]

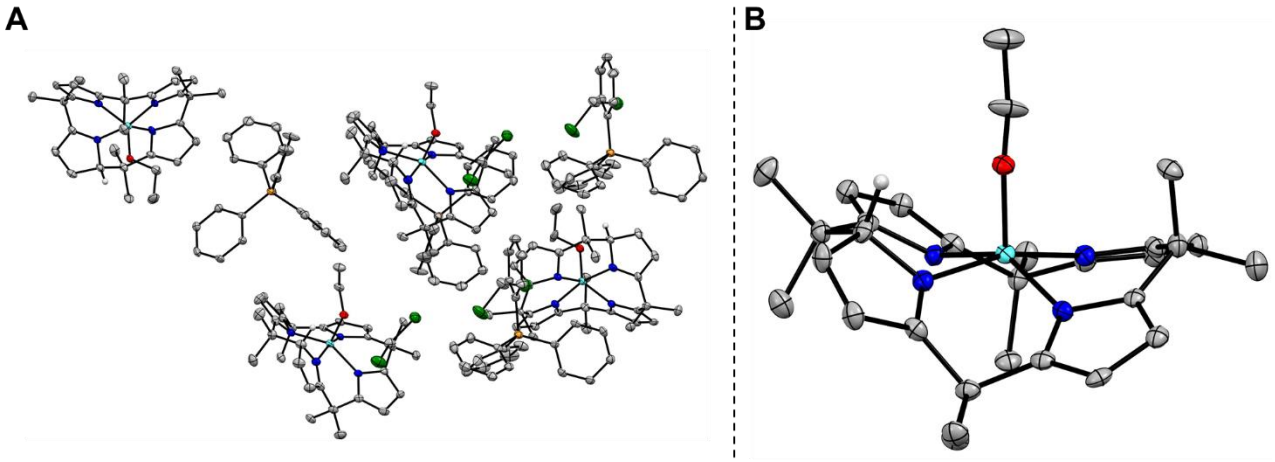


Figure S-32: A) Asymmetric unit of the crystal lattice found for [PPh_4][(EtO)-**1***-H], and **B)** molecular structure of the respective anion, [(EtO)-**1***-H]$^-$. All hydrogen atoms except for the one which was transferred to the ligand backbone are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.

Only molecular connectivity could be determined due to poor diffraction.

Table S-7: Crystal data and structure refinement for [PPh_4][(EtO)-**1***-H] (mo_lms40_0m).

Identification code	mo_lms40_0m
Empirical formula	$C_{100}H_{120}Al_2Cl_4N_8O_2P_2$
Formula weight	1843.93
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	19.4778(18)
b/Å	20.0474(18)
c/Å	28.343(2)
α/°	73.969(2)
β/°	78.374(3)
γ/°	85.119(3)
Volume/Å^3	10413.8(16)
Z	8
ρ_{calc}g/cm^3	1.176
μ/mm^{-1}	0.213
F(000)	3904.0

Crystal size/mm^3	0.104 × 0.093 × 0.082
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.74 to 50
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -33 ≤ l ≤ 33
Reflections collected	437465
Independent reflections	36658 [R_{int} = 0.0754, R_{sigma} = 0.0313]
Data/restraints/parameters	36658/0/2341
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1377
Final R indexes [all data]	R_1 = 0.0990, wR_2 = 0.1728
Largest diff. peak/hole / e Å^{-3}	0.69/-0.96

[PPh_4]$_2$[(EtO)-**1**]

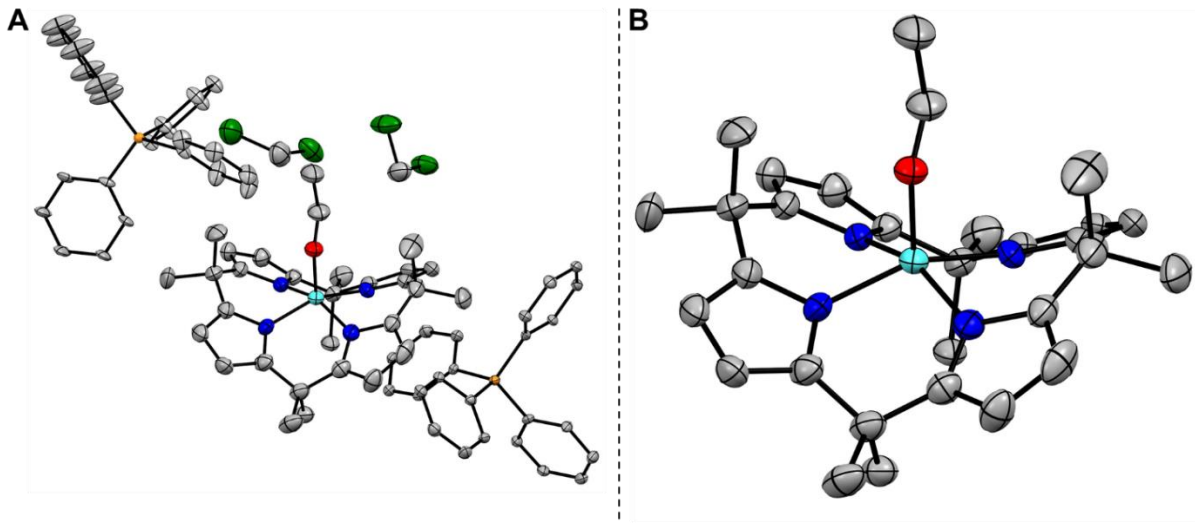


Figure S-33: A) Asymmetric unit of the crystal lattice found for [PPh_4]$_2$[(EtO)-**1**], and **B)** molecular structure of the respective dianion, [(EtO)-**1**]$^{2-}$. Hydrogen atoms are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.

Only molecular connectivity could be determined due to poor diffraction.

Table S-8: Crystal data and structure refinement for [PPh_4]$_2$[(EtO)-**1**] (mo_lms045_0m).

Identification code	mo_lms045_0m
Empirical formula	$C_{80}H_{81}AlCl_4N_4OP_2$
Formula weight	1345.28
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.9549(12)
b/Å	12.7424(13)
c/Å	25.639(3)
α/°	86.841(3)
β/°	76.942(3)
γ/°	70.049(3)
Volume/Å^3	3575.3(6)
Z	2
ρcalcg/cm^3	0.935
μ/mm^{-1}	0.232

F(000)	1060.0
Crystal size/mm^3	0.214 × 0.133 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.104 to 50.264
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30
Reflections collected	66848
Independent reflections	12646 [R_{int} = 0.1210, R_{sigma} = 0.0851]
Data/restraints/parameters	12646/335/786
Goodness-of-fit on F2	1.445
Final R indexes [I>=2σ (I)]	R_1 = 0.1435, wR_2 = 0.3843
Final R indexes [all data]	R_1 = 0.2086, wR_2 = 0.4313
Largest diff. peak/hole / e Å^{-3}	1.47/-1.04

S-13. Computational details

For all quantum chemical calculations Orca 4.0.1, 4.1.2, or 4.2.1[14] was employed using the computational resources of the bwUniCluster at the Karlsruhe Institute of Technology or those of the bwForClusters JUSTUS or JUSTUS2 at Ulm University within the Baden-Württemberg High Performance Computing program.

All equilibrium structures were obtained with the following key word line and were confirmed to possess only positive Hessian matrix eigenvalues.

```
! RKS PBEh-3c Grid5 TightSCF OPT FREQ
```

PBEh-3c[15] is a composite electronic structure method based on the Perdew-Burke-Ernzerhoff (PBE) exchange-correlation functional combined with polarized valence-double zeta Gaussian atomic orbital basis sets (def2-mSVP). It further accounts for basis set superposition errors with the geometrical counterpoise scheme (gCP)[16], and for London dispersion interactions with the Becke-Johnson-damped D3 correction[17, 18]. It is especially suited for structure calculations of small and medium-sized molecules and produces results similar to those obtained with MP2/def2-TZVPP, while being much less computationally demanding.[19]

Transition structures were optimized toward a single negative Hessian matrix eigenvalue with

```
! RKS PBEh-3c Grid5 TightSCF SlowConv OptTS FREQ

%geom

   Calc_Hess true

end
```

It was ensured that the correct first-order saddle point on the potential energy surface was located by animation of the imaginary frequency in Chemcraft.[20]

All final gas phase single point energies were calculated with:

```
! RKS PW6B95 def2-QZVPP D3 ABC RIJCOSX AutoAux grid5 finalgrid7 gridx6 TightSCF
```

PW6B95[21] is a hybrid meta exchange-correlation functional and was combined with the large def2-QZVPP basis set[22]. The D3 scheme with Becke-Johnson damping including three-body contributions (ABC) was

applied. The RIJCOSX Fock-matrix formation algorithm was used as it is implemented in Orca along with the respective automatically generated auxiliary basis sets (AutoAux)[23]. The RIJCOSX scheme combines the chain of spheres exchange approximation (COSX)[24] for the computation of the exchange matrix with the Split-RI-J algorithm[25] for the calculation of the Coulomb matrix.

Enthalpies at 298.15 K were calculated with the total thermal and zero-point energy correction from the PBEh-3c calculation combined with the electronic single point energies obtained on the PW6B95-D3(BJ)/def2-QZVPP level of theory with the PBEh-3c structures. For Gibbs free energies, the enthalpy values were merged with the vibrational entropy terms calculated on the PBEh-3c level according to the rigid-rotor-harmonic-oscillator approximation (QRRHO) of Grimme.[26]

The influence of a solvating environment on the Gibbs free energy at 298.15 K was taken into account with Klamt's conductor like screening model for real solvents (COSMO-RS)[27-29] as it is implemented[30] in the Amsterdam Modeling suite (ADF 2019.103)[31]. All ADF-preset parameters were used, and the maximum number of iterations in the geometry convergence section was set to zero. COSMO-RS correction for enthalpies was achieved by calculating ΔG-corrections at five different temperatures (278.15, 288.15, 298.15, 308.15, 318.15 K). Satisfying $\Delta G = \Delta H - T\Delta S$, the plot of the obtained Gibbs free energy corrections against the temperature allows to fit a straight line from which the corrections for ΔH were extracted.

Ball and stick representations were rendered with Chemcraft 1.8[20], molecular orbitals with IboView.[32]

S-14. Computational investigation of the addition reaction

The addition reaction of protic substrates to [**1**]$^-$ (Scheme S-3) was studied at the PW6B95-D3(BJ)/def-QZVPP//PBEh-3c level of theory. The influence of dichloromethane as solvent was taken into account with the COSMO-RS method. The following thermodynamic parameters were obtained.

Table S-9: Calculated reaction enthalpies and Gibbs free reaction enthalpies for the addition reaction of protic substrates to [**1**]$^-$.

Substrate	$\Delta_R H_{DFT}$ [kJ mol^{-1}]	$\Delta_R G_{DFT}$ [kJ mol^{-1}]
^{t}BuOH	−48.3	2.4
(*p*-MeOPh)$_2$CHOH	−57.7	−12.4
^{i}PrOH	−60.9	−14.4
p-MeBnOH	−75.9	−17.7
EtOH	−65.9	−23.5
p-NO$_2$BnOH	−83.0	−33.9
BzOH	−100.9	−48.2
p-BrPhOH	−97.2	−49.6

For isopropanol, the full reaction coordinate was investigated by DFT (PW6B95-D3(BJ)/def-QZVPP//PBEh-3c). It accords with the experimental observations.

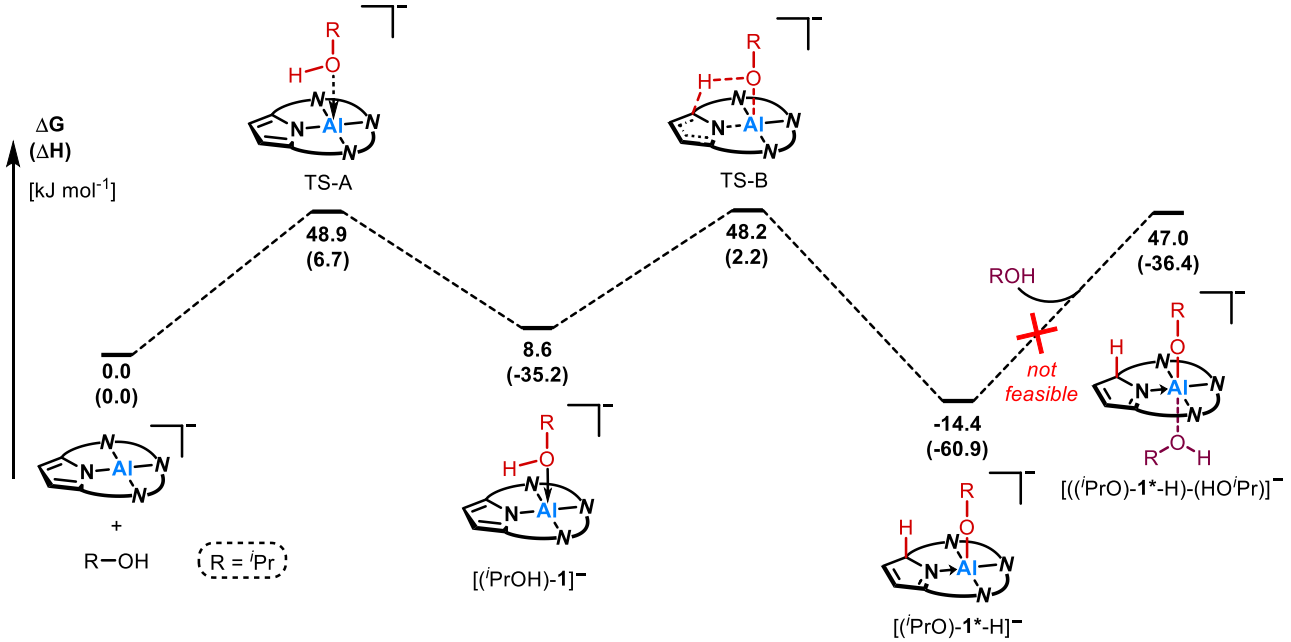


Figure S-34: Calculated reaction pathway for the addition of isopropanol to [**1**]⁻. The ball and stick representation of all structures are given in Chapter S-18.

S-15. Computational investigation of [1,5]H sigmatropic rearrangements in [(EtO)-1*-H]⁻

In Chapter S-7, a mechanistic suggestion for the H/D scrambling, which was observed when [**1**]⁻ was treated with EtOD, is given. The proposed mechanism comprises a series of [1,5]H/D sigmatropic shiftings. All involved tautomers and the respective transition states were studied at the PW6B95-D3(BJ)/def-QZVPP//PBEh-3c level of theory. The influence of dichloromethane as solvent was taken into account with the COSMO-RS method.

Path A

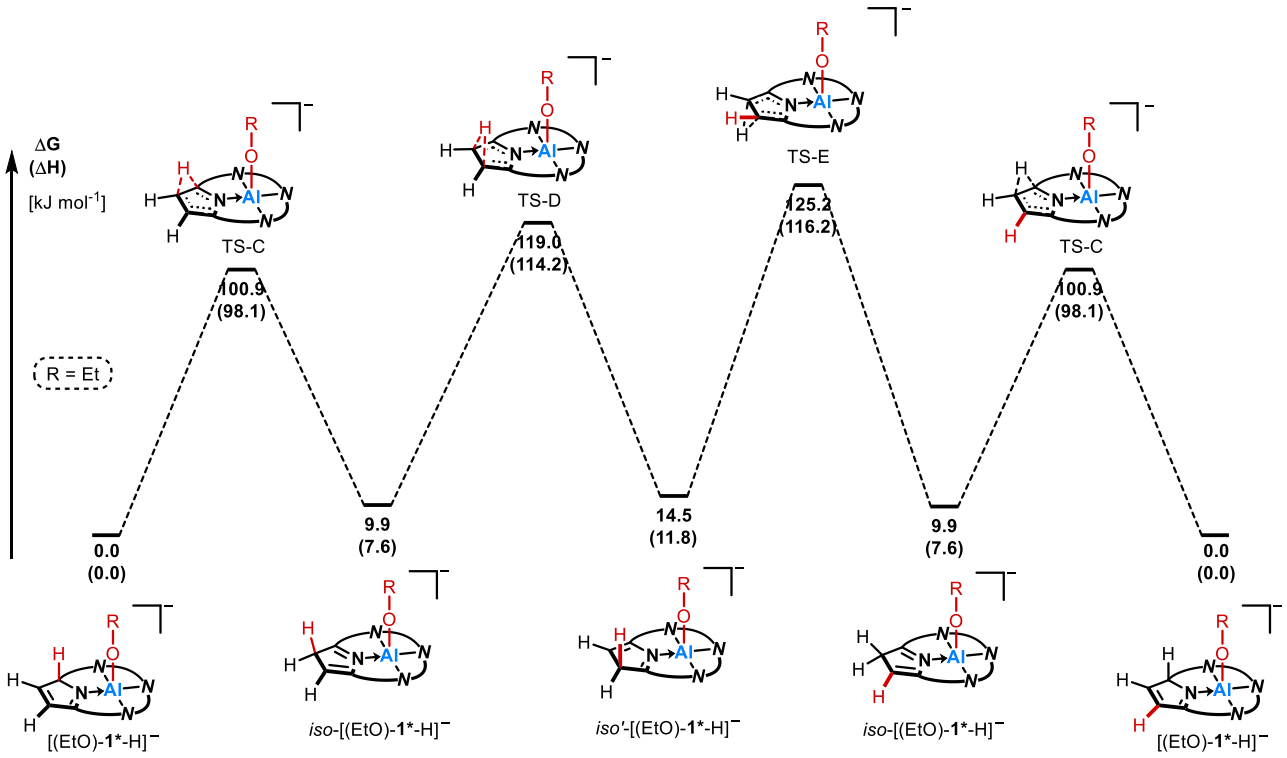


Figure S-35: Calculated reaction pathway for the cascade of [1,5]H/D sigmatropic rearrangements observed within [(EtO)-**1***-H/D]⁻ following path A (*c.f.* Scheme S-7). The ball and stick representation of all structures are given in Chapter S-18.

Path B

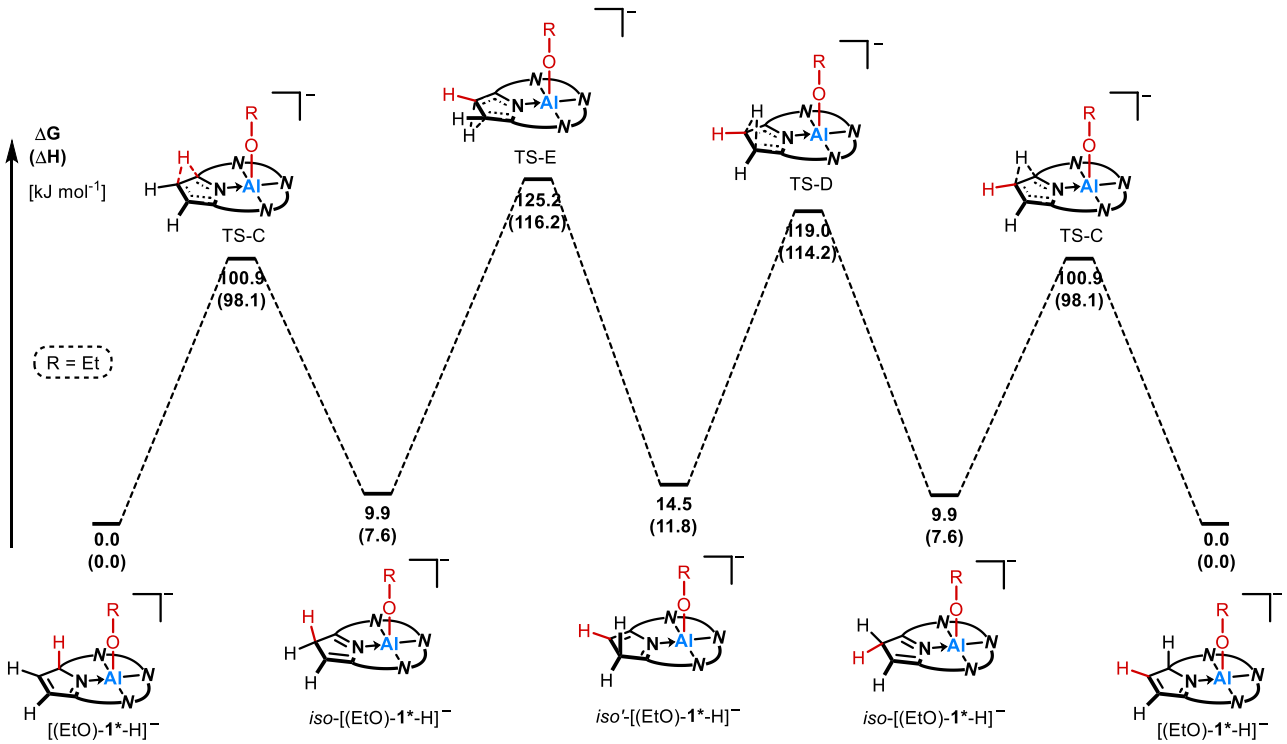


Figure S-36: Calculated reaction pathway for the cascade of [1,5]H/D sigmatropic rearrangements observed within [(EtO)-**1***-H/D]⁻ following path B (*c.f.* Scheme S-7). The ball and stick representation of all structures are given in Chapter S-18.

Non-productive path

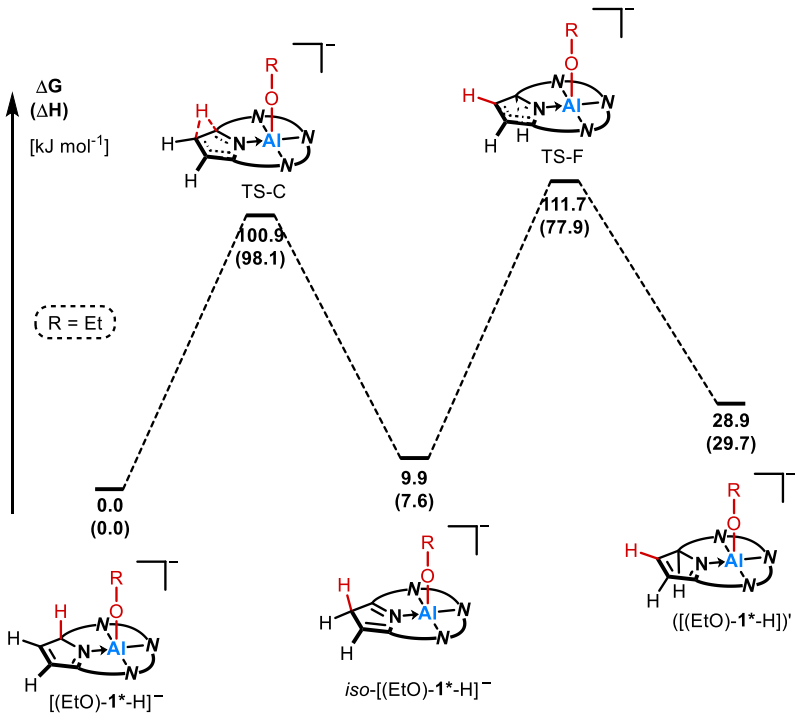
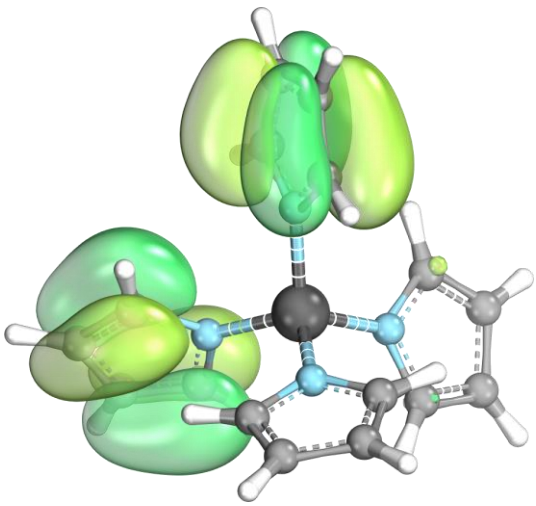


Figure S-37: Calculated reaction pathway for the cascade of [1,5]H/D sigmatropic rearrangements observed within [(EtO)-**1***-H/D]⁻ following the non-productive path (*c.f.* Scheme S-7). The ball and stick representation of all structures are given in Chapter S-18.

S-16. Visualization of the Kohn-Sham frontier molecular orbitals of the tetrapyrrolato aluminate and of [1]⁻

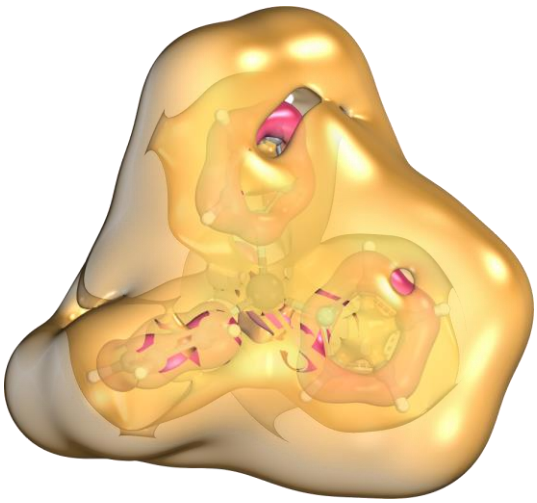
The visualization of the Kohn-Sham frontier molecular orbitals of the tetrapyrrolato aluminate and of [**1**]⁻ was done using the wavefunction calculated on the PW6B95-D3(BJ)/def-QZVPP//PBEh-3c level (isosurface threshold: 80.00, resolution: 12.00 Å⁻¹).

[Al(pyrrolato)$_4$]⁻



HOMO

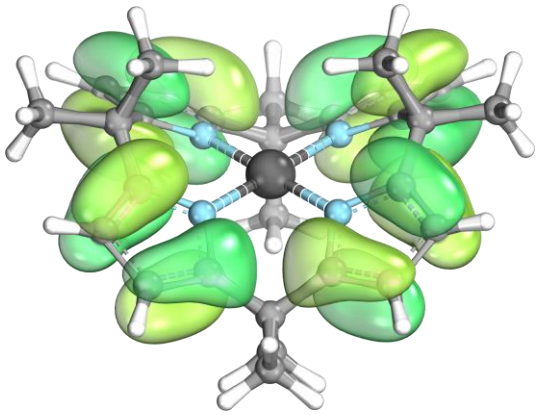
-2.9246 eV



LUMO

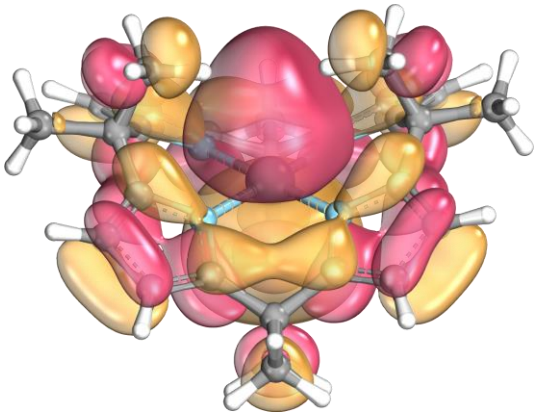
3.4800 eV

[1]$^-$



HOMO

-2.4257 eV



LUMO

2.2200 eV

S-17. NMR spectra

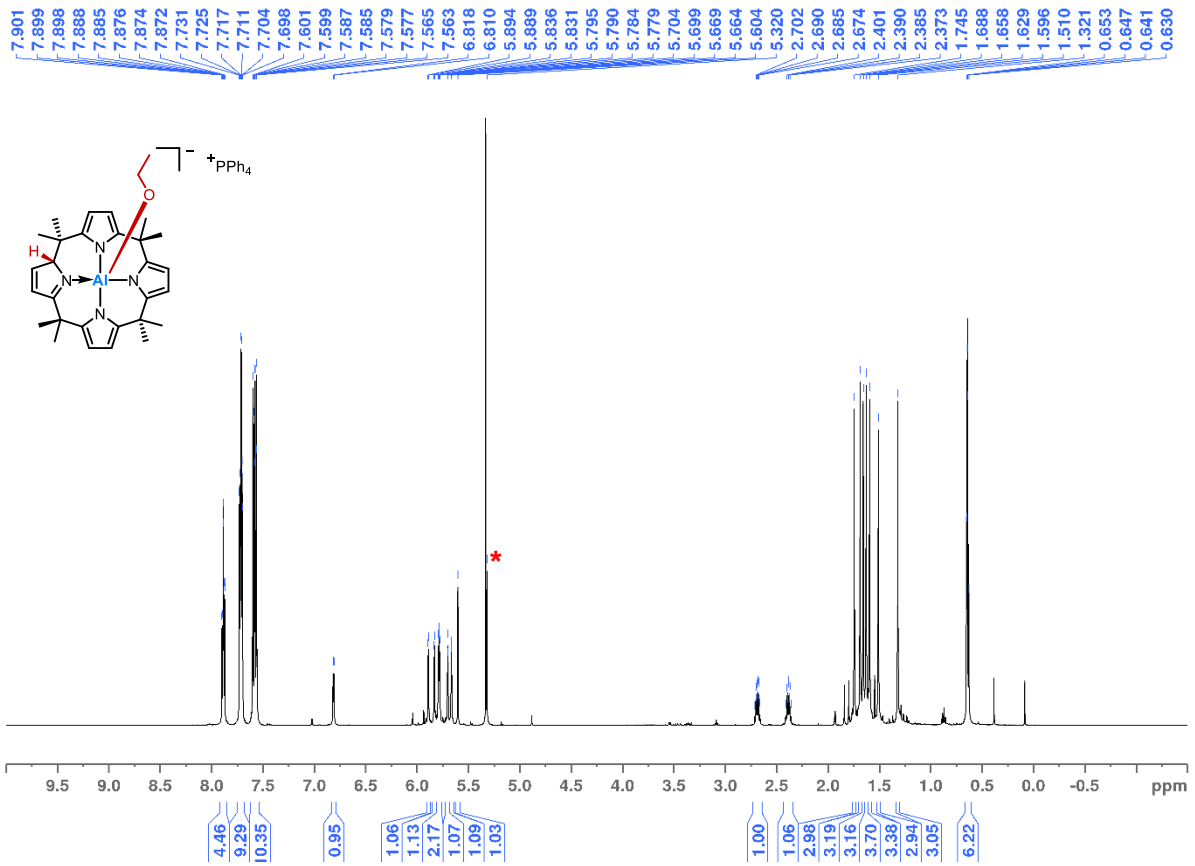


Figure S-38: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of $[PPh_4][$(EtO)-**1***-H]. The $[PPh_4][$(EtO)-**1***-H] / (EtO)-**1****-HH ratio was calculated to 26:1. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4][$**1**], are marked with a red asterisk.

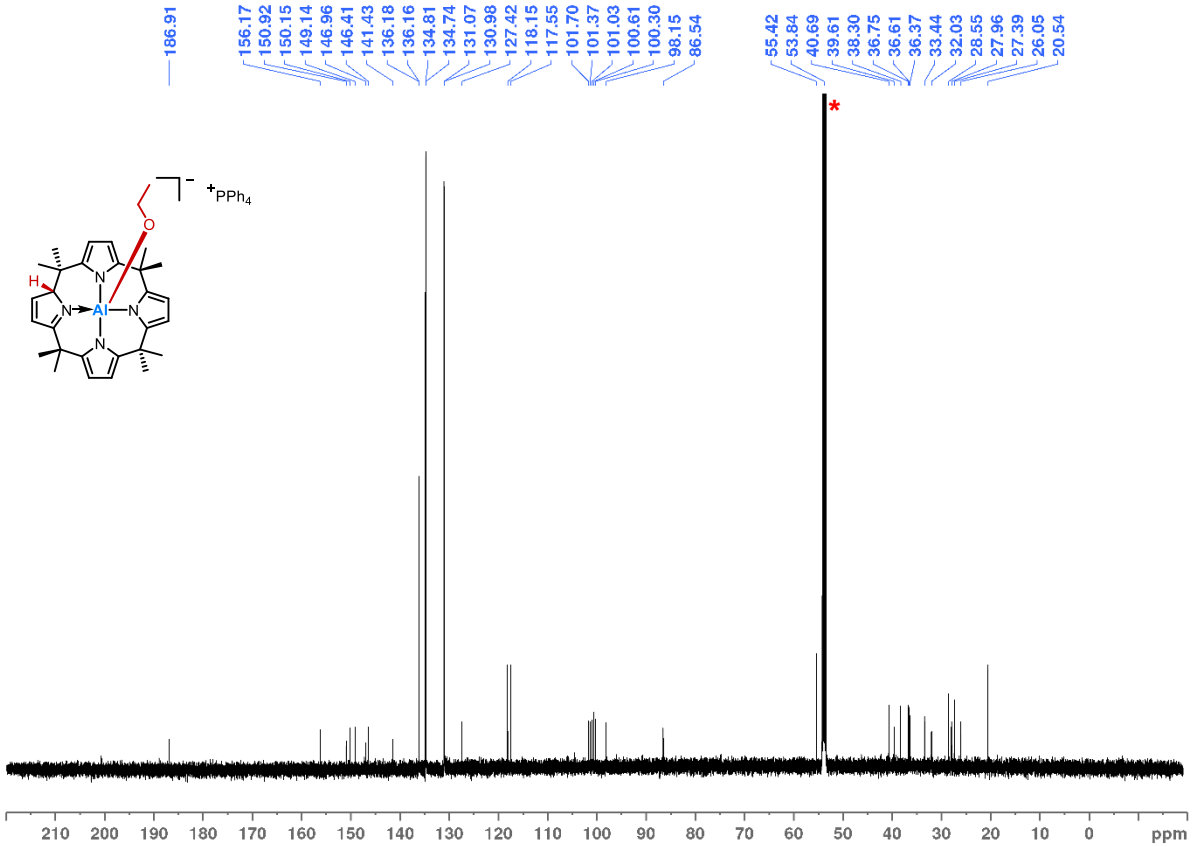


Figure S-39: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of $[PPh_4][$(EtO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4][$**1**], are marked with a red asterisk.

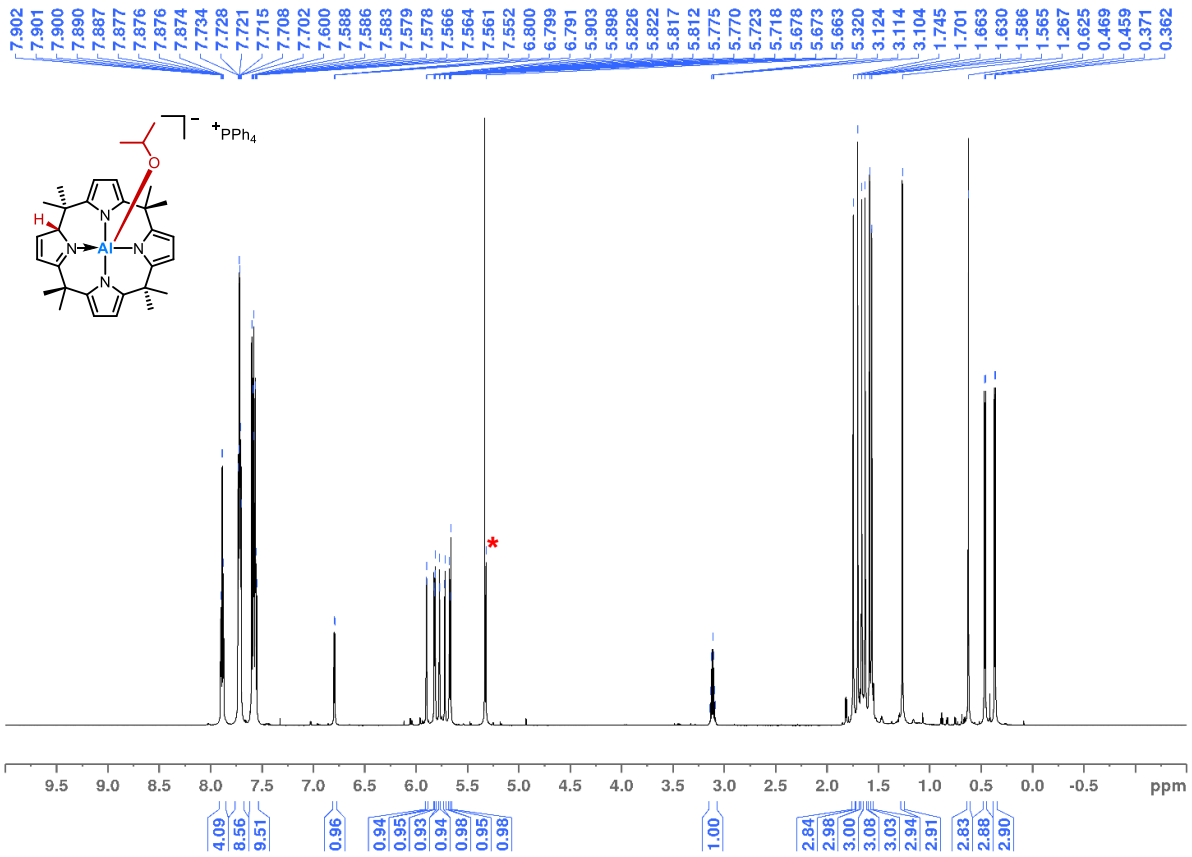


Figure S-40: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of $[PPh_4][(^{i}PrO)$-**1***-H]. The $[PPh_4][(^{i}PrO)$-**1***-H] / (^{i}PrO)-**1****-HH ratio was calculated to 38:1. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4]$[**1**], are marked with a red asterisk.

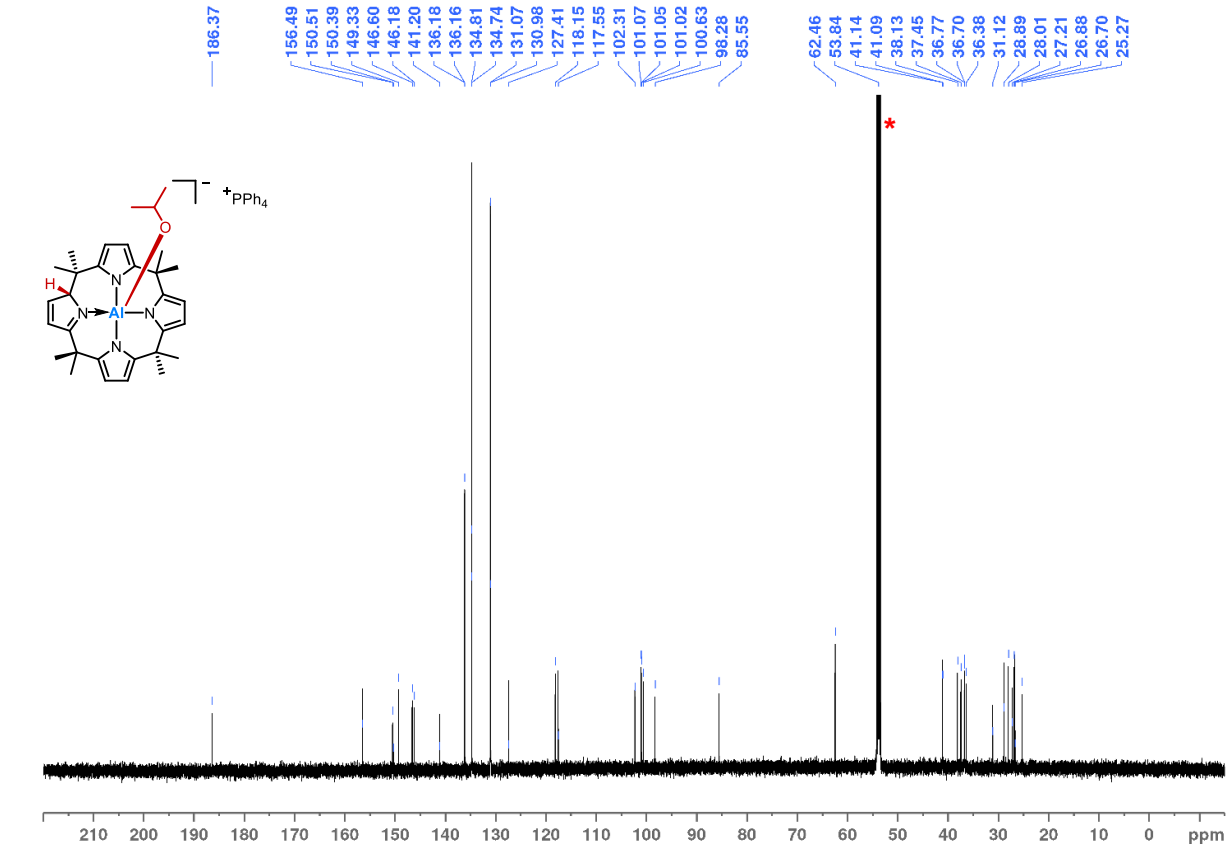


Figure S-41: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of $[PPh_4][(^{i}PrO)$-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4]$[**1**], are marked with a red asterisk.

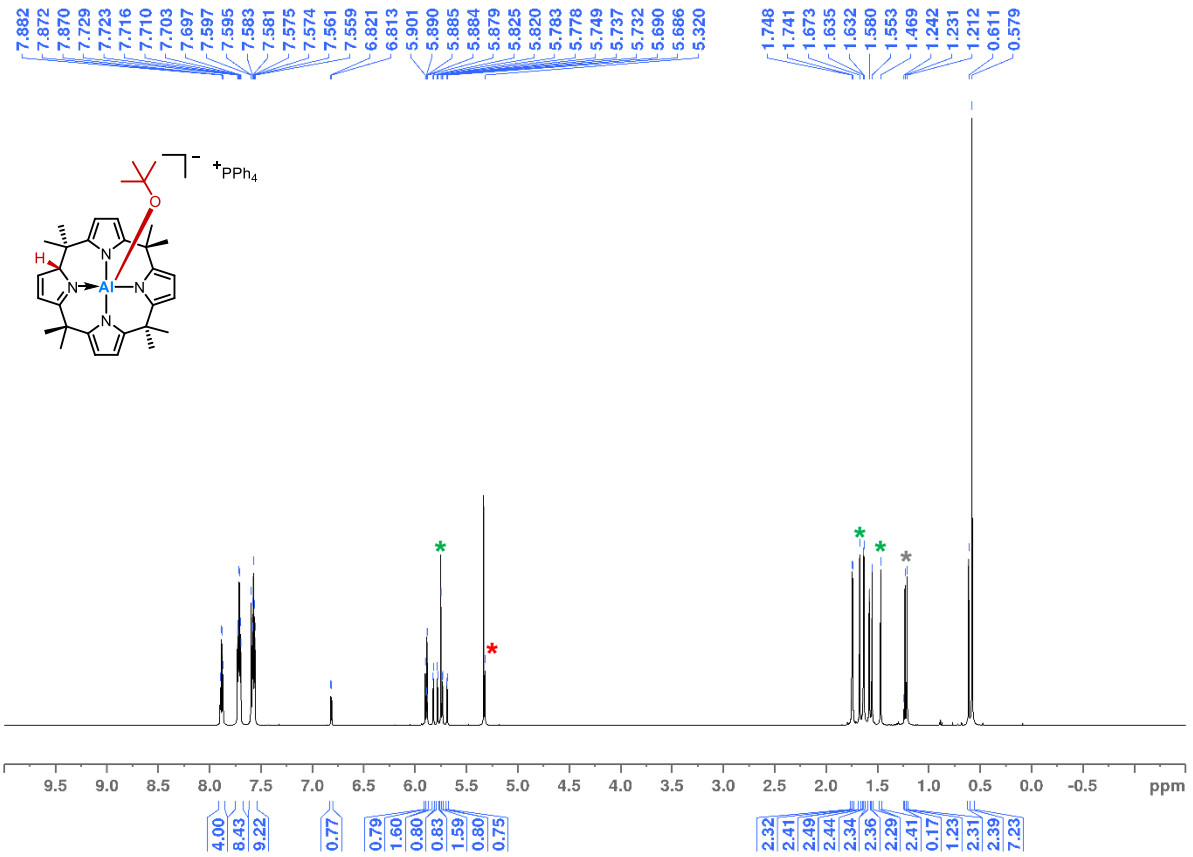


Figure S-42: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(^{t}BuO)-**1***-H]. The addition reaction with ^{t}BuOH is not quantitative. Free [**1**]$^-$ is marked with green, free ^{t}BuOH with gray asterisks. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

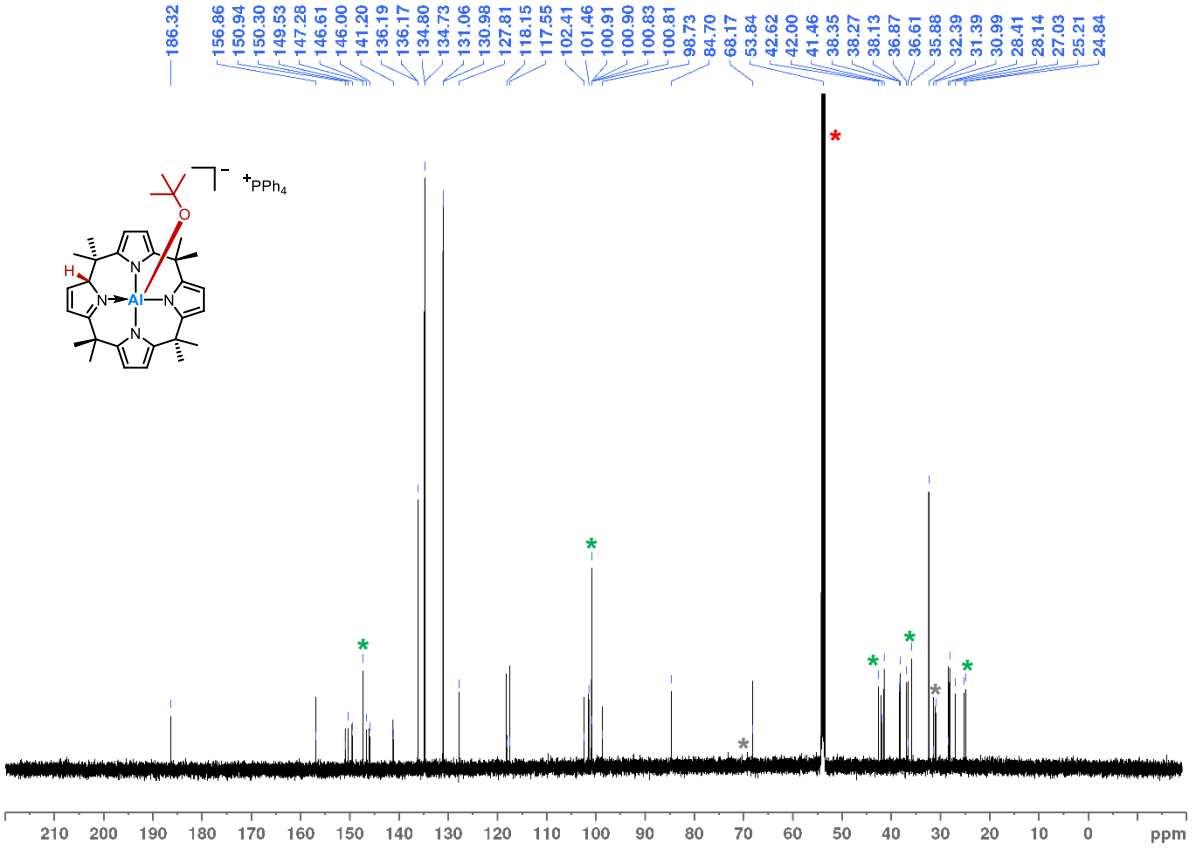


Figure S-43: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of [PPh_4][(^{t}BuO)-**1***-H]. The addition reaction with ^{t}BuOH is not quantitative. Free [**1**]$^-$ is marked with green, free ^{t}BuOH with gray asterisks. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

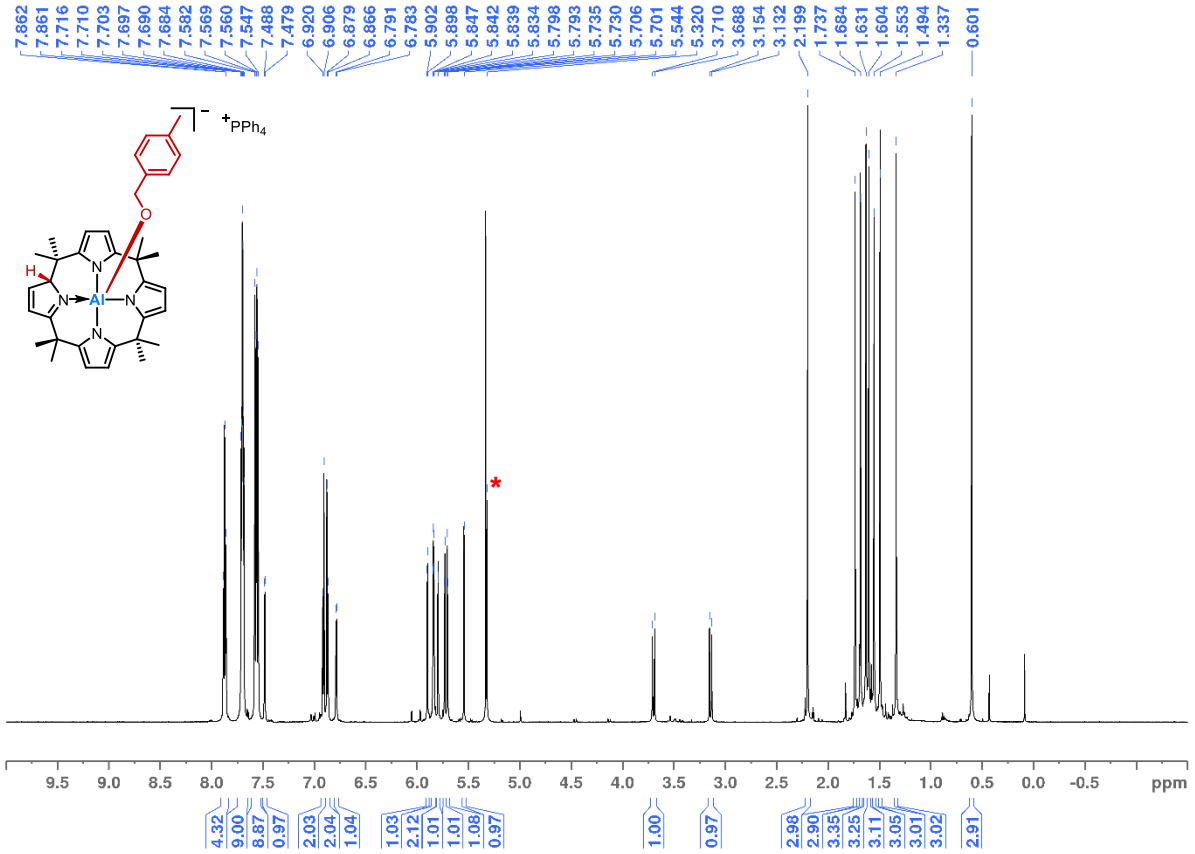


Figure S-44: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-MeBnO)-**1***-H]. The [PPh_4][(*p*-MeBnO)-**1***-H] / (*p*-MeBnO)-**1****-HH ratio was calculated to 32:1. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

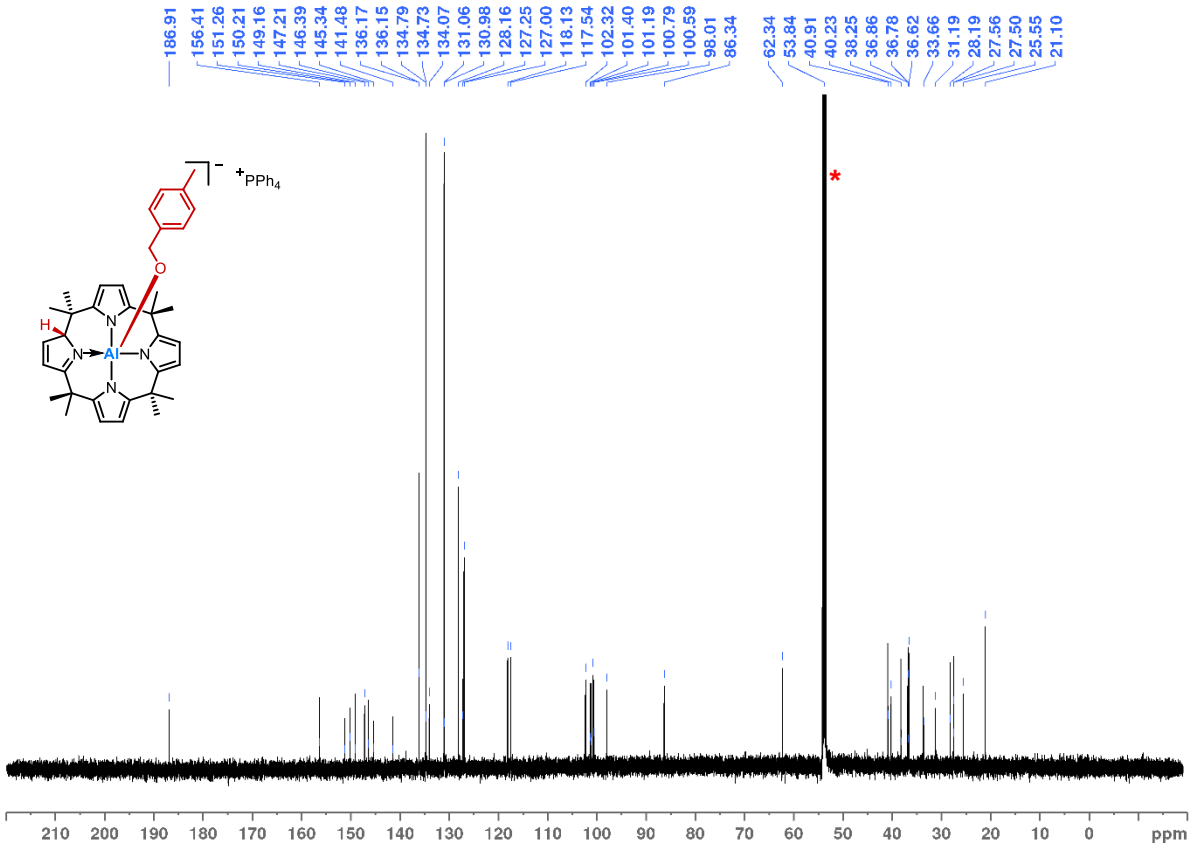


Figure S-45: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-MeBnO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

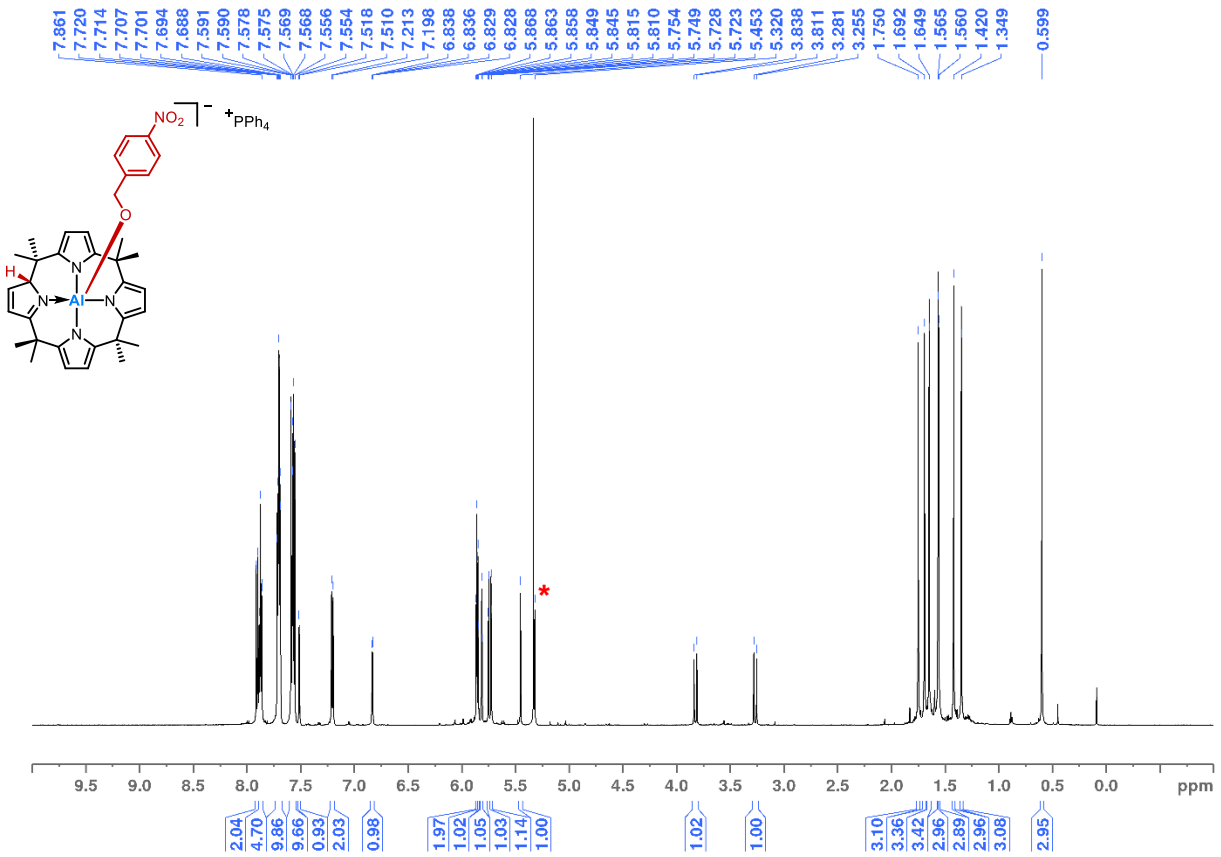


Figure S-46: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-NO_2BnO)-**1***-H]. The [PPh_4][(*p*-NO_2BnO)-**1***-H] / (*p*-NO_2BnO)-**1****-HH ratio was calculated to 46:1. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

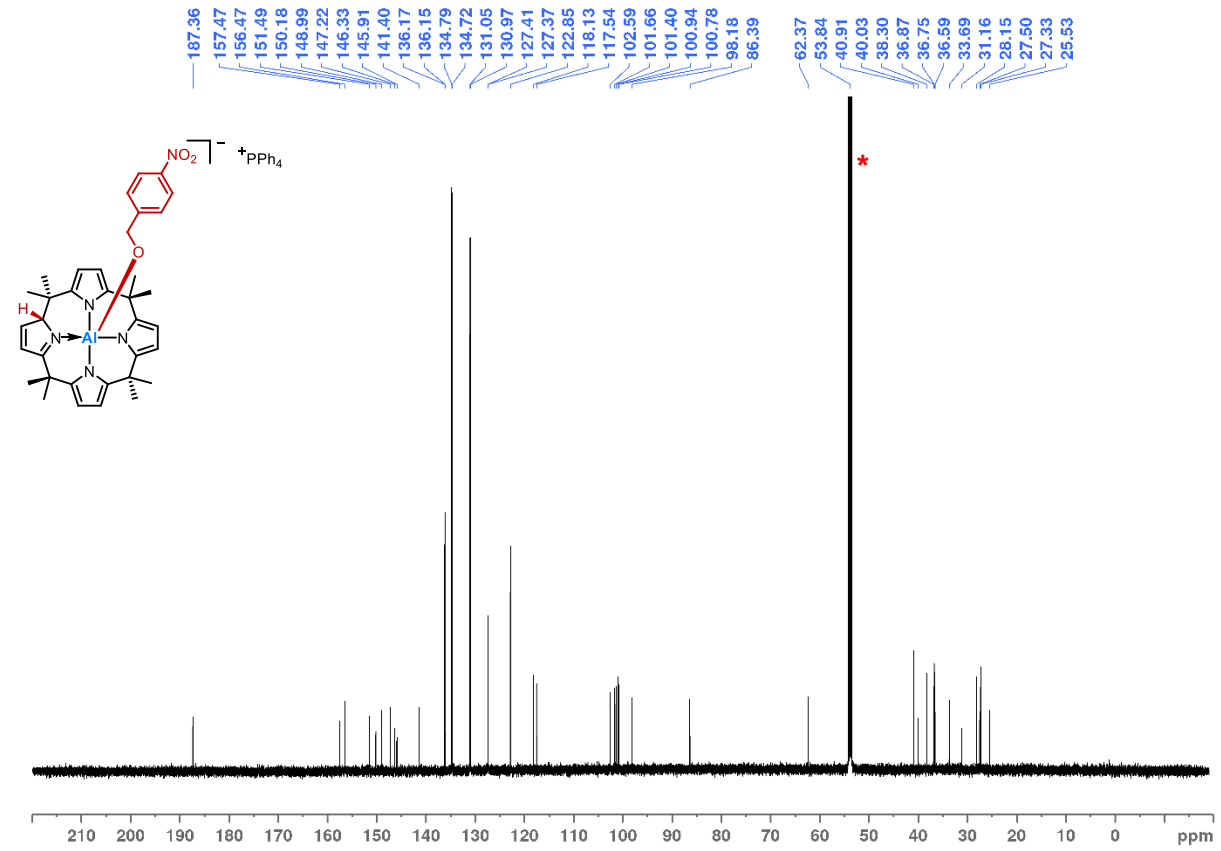


Figure S-47: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-NO_2BnO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

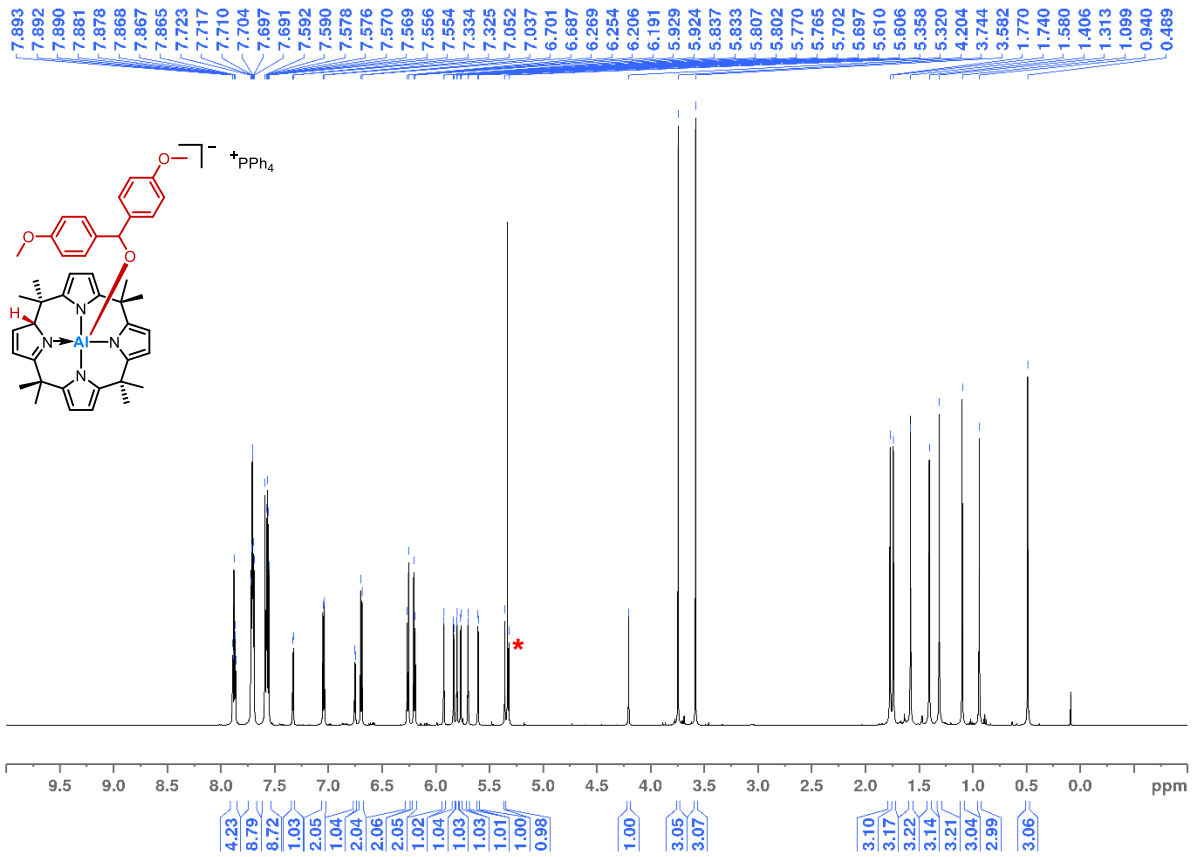


Figure S-48: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][((*p*-MeOPh)$_2$CHO)-**1***-H]. Indication of the formation of ((*p*-MeOPh)$_2$CHO)-**1****-HH was not found. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

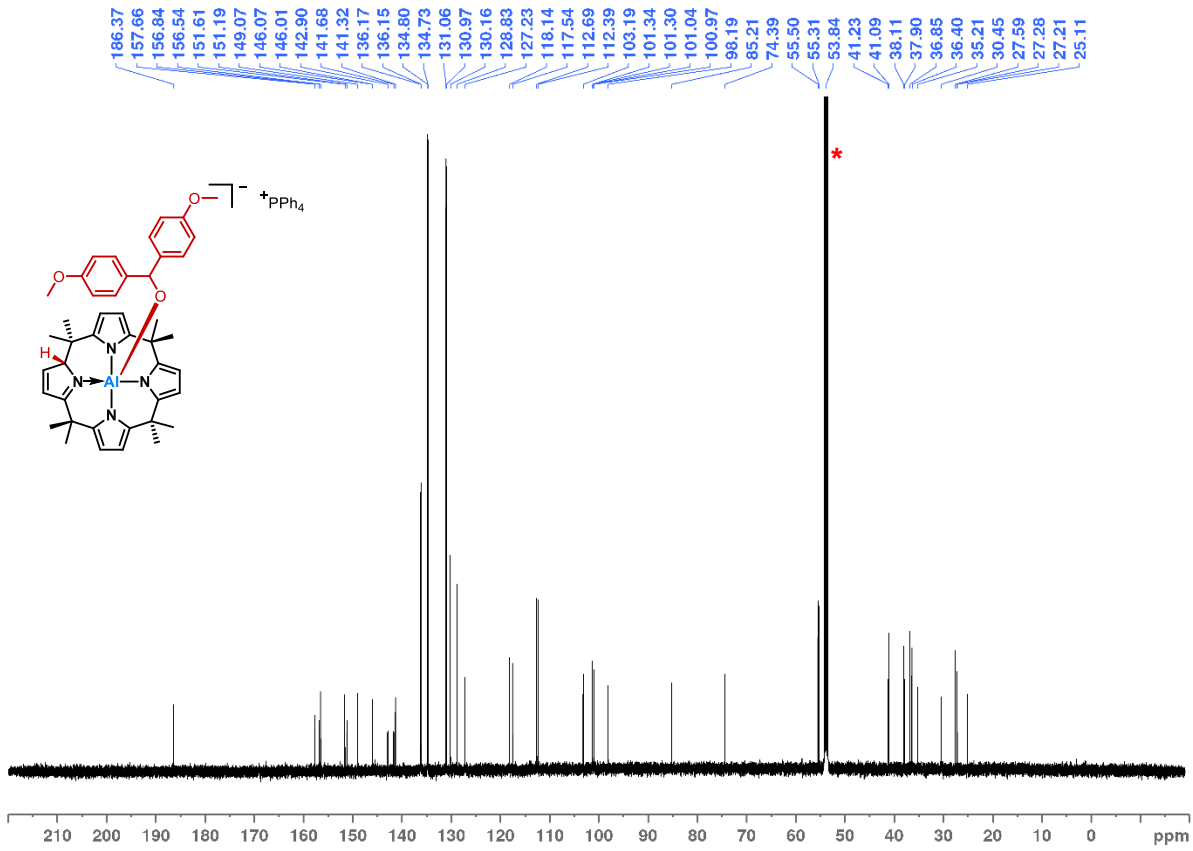


Figure S-49: ^{13}C{^{1}H} NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of [PPh_4][((*p*-MeOPh)$_2$CHO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

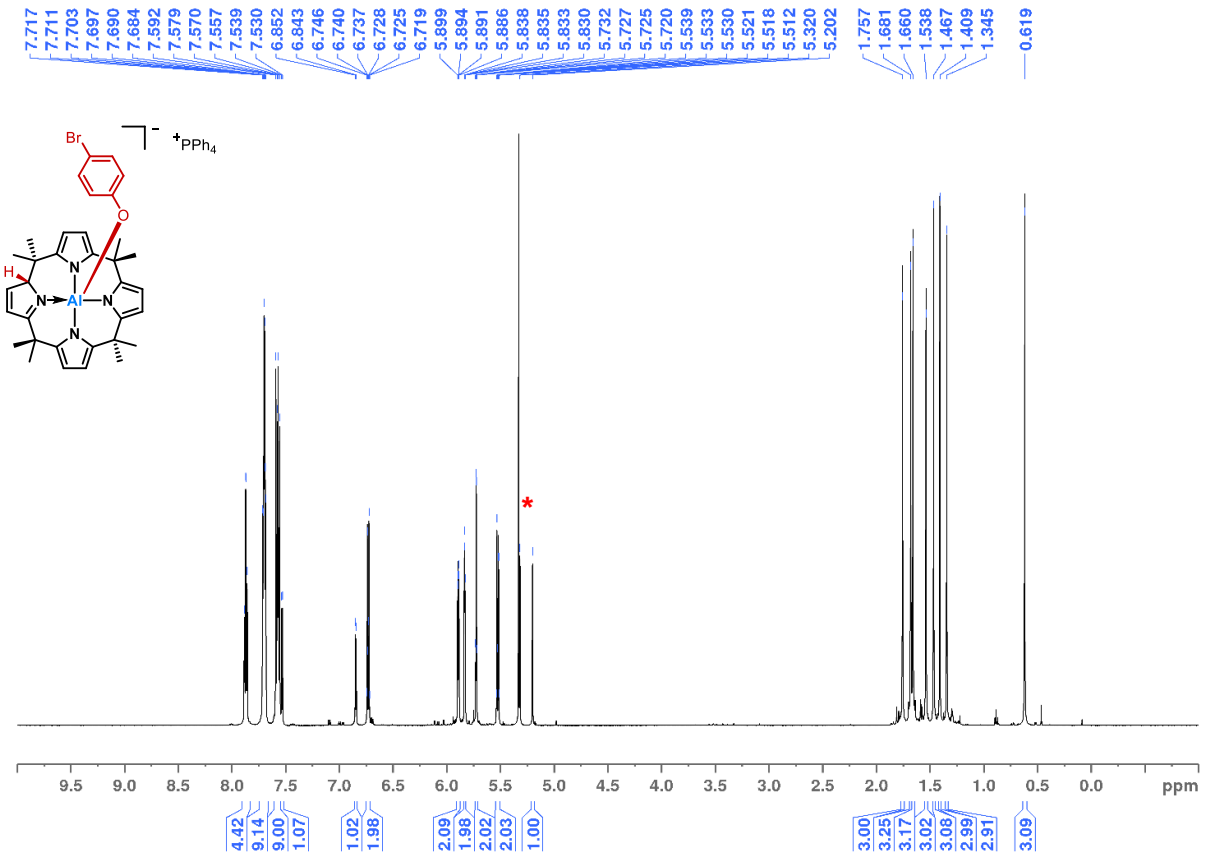


Figure S-50: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-BrPhO)-**1***-H]. The [PPh_4][(*p*-BrPhO)-**1***-H] / (*p*-BrPhO)-**1****-HH ratio was calculated to 60:1. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

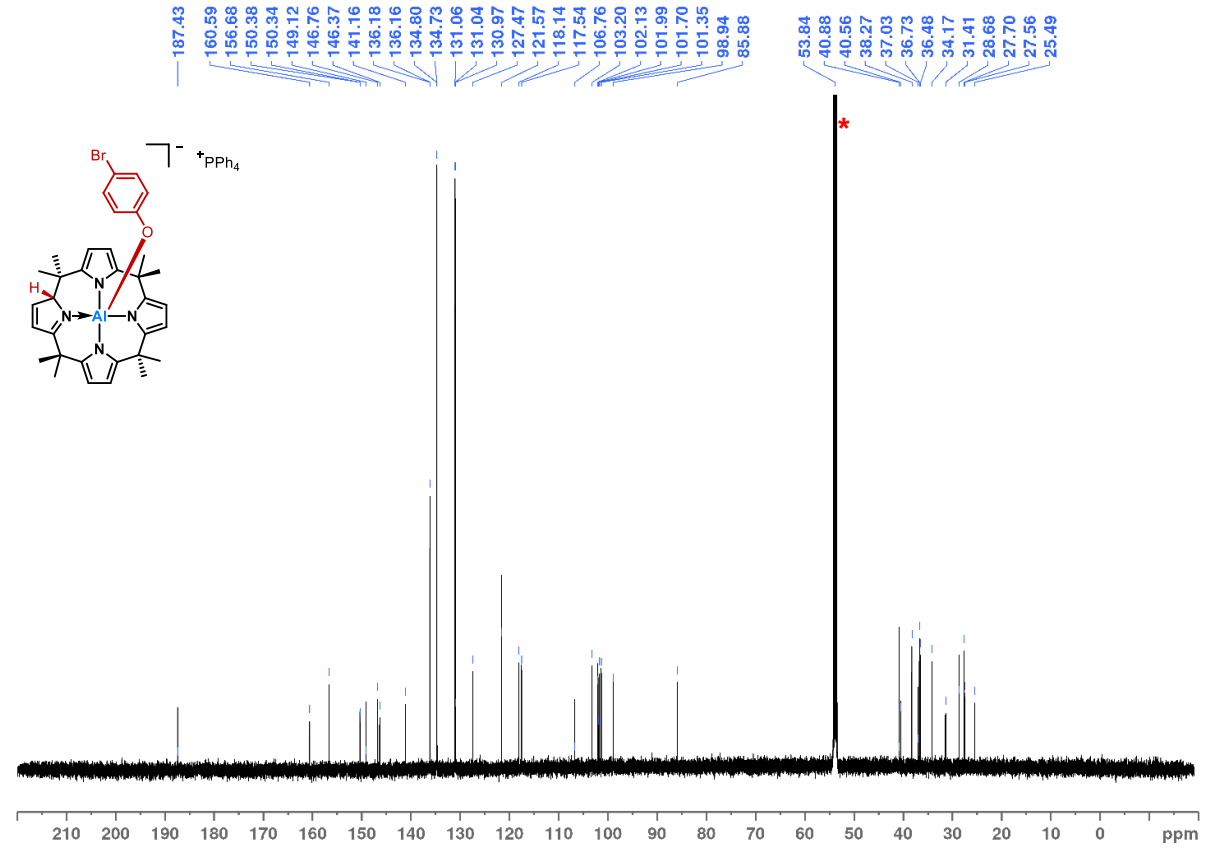


Figure S-51: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of [PPh_4][(*p*-BrPhO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

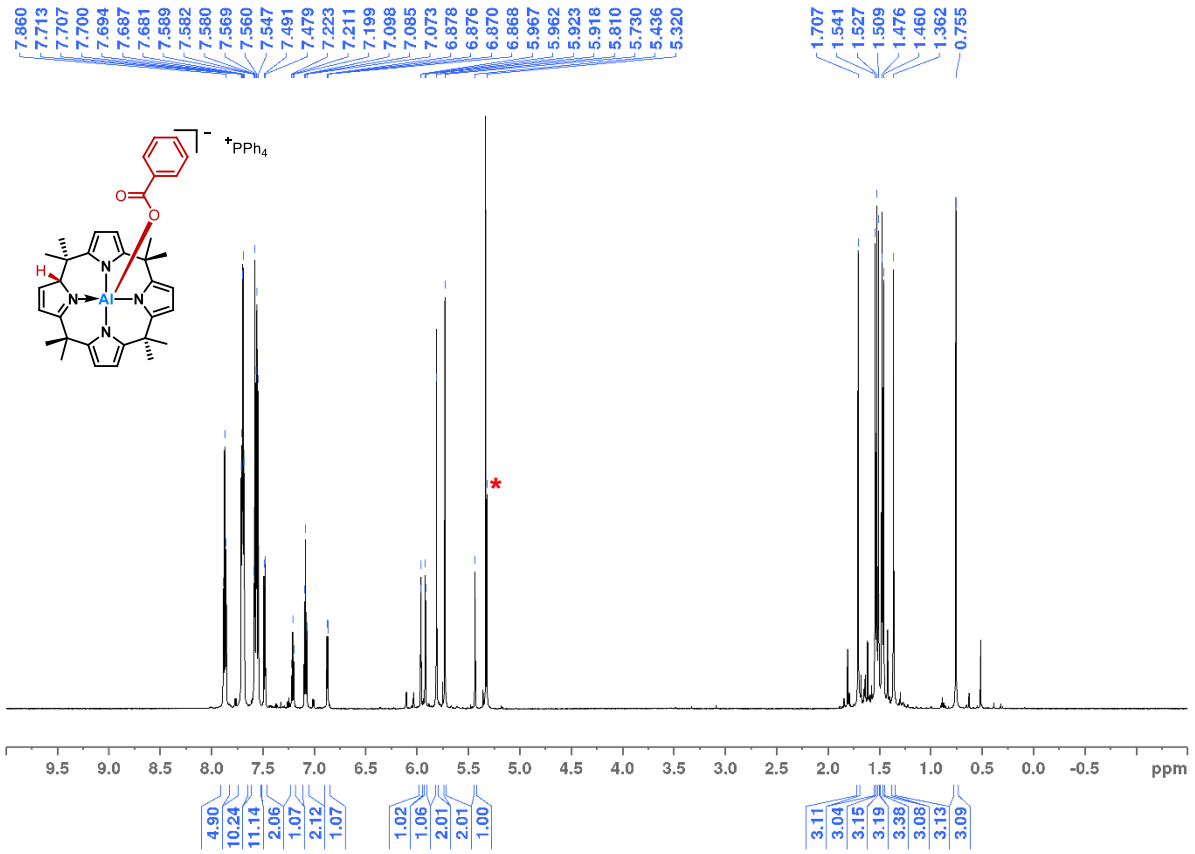


Figure S-52: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(BzO)-**1***-H]. The [PPh_4][(BzO)-**1***-H] / (BzO)-**1****-HH ratio was calculated to 16:1. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

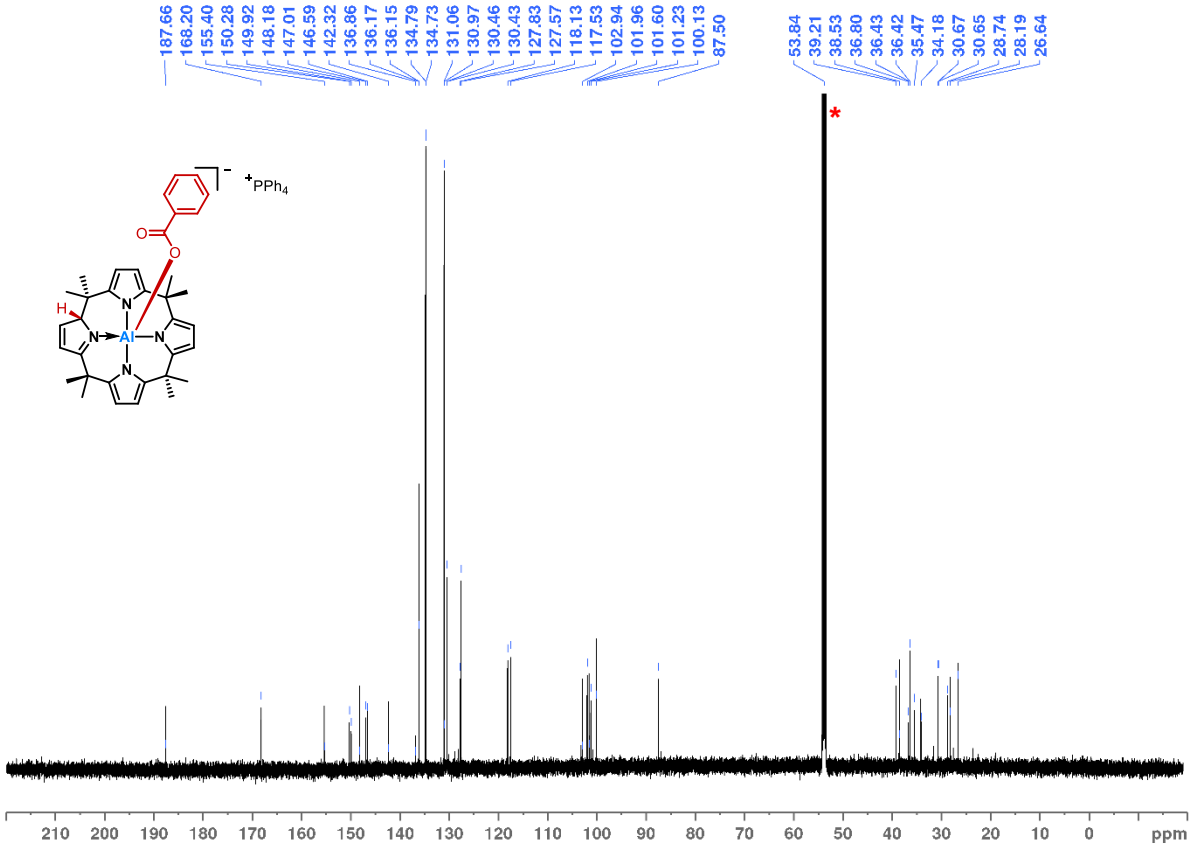


Figure S-53: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of [PPh_4][(BzO)-**1***-H]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

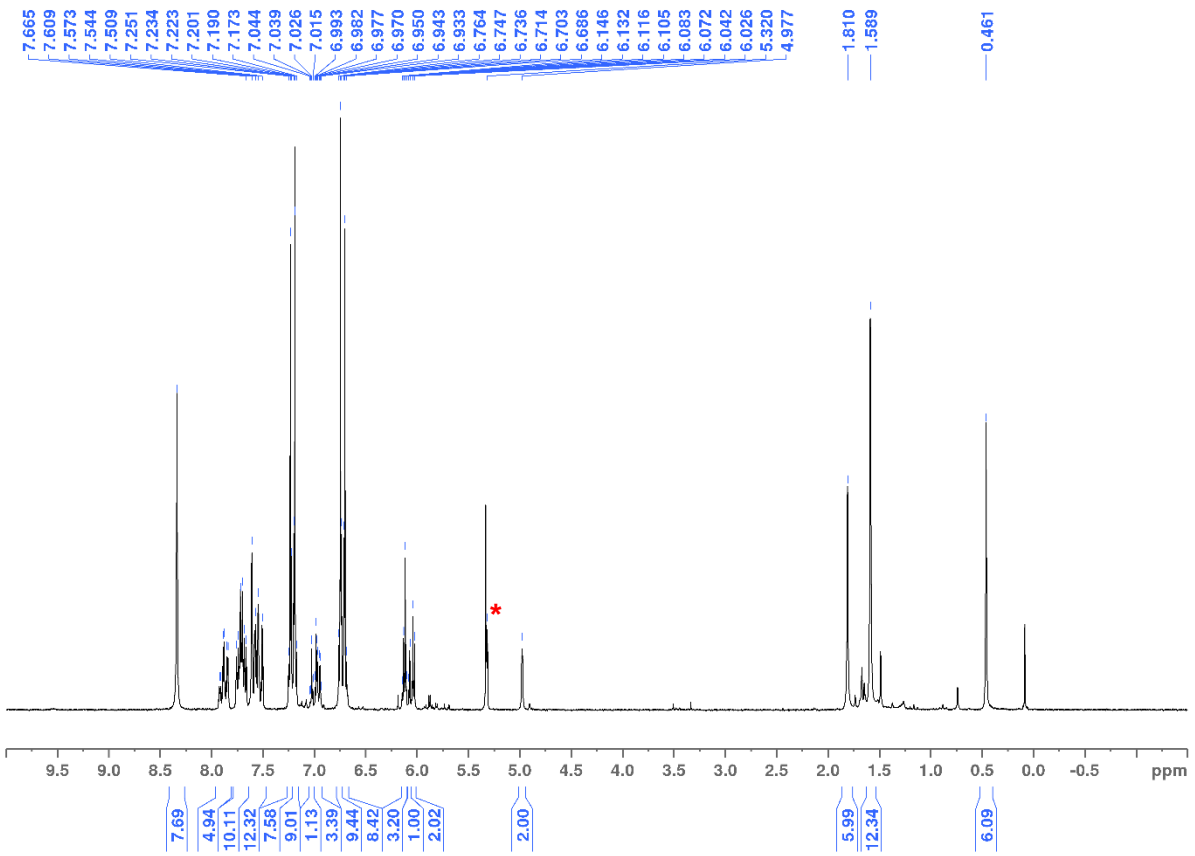


Figure S-54: ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 298 K) of [PPh_4][**1**] treated with an excess of *p*-BrPhOH. This resulted in the formation of the neutral (*p*-BrO)-**1****-HH. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

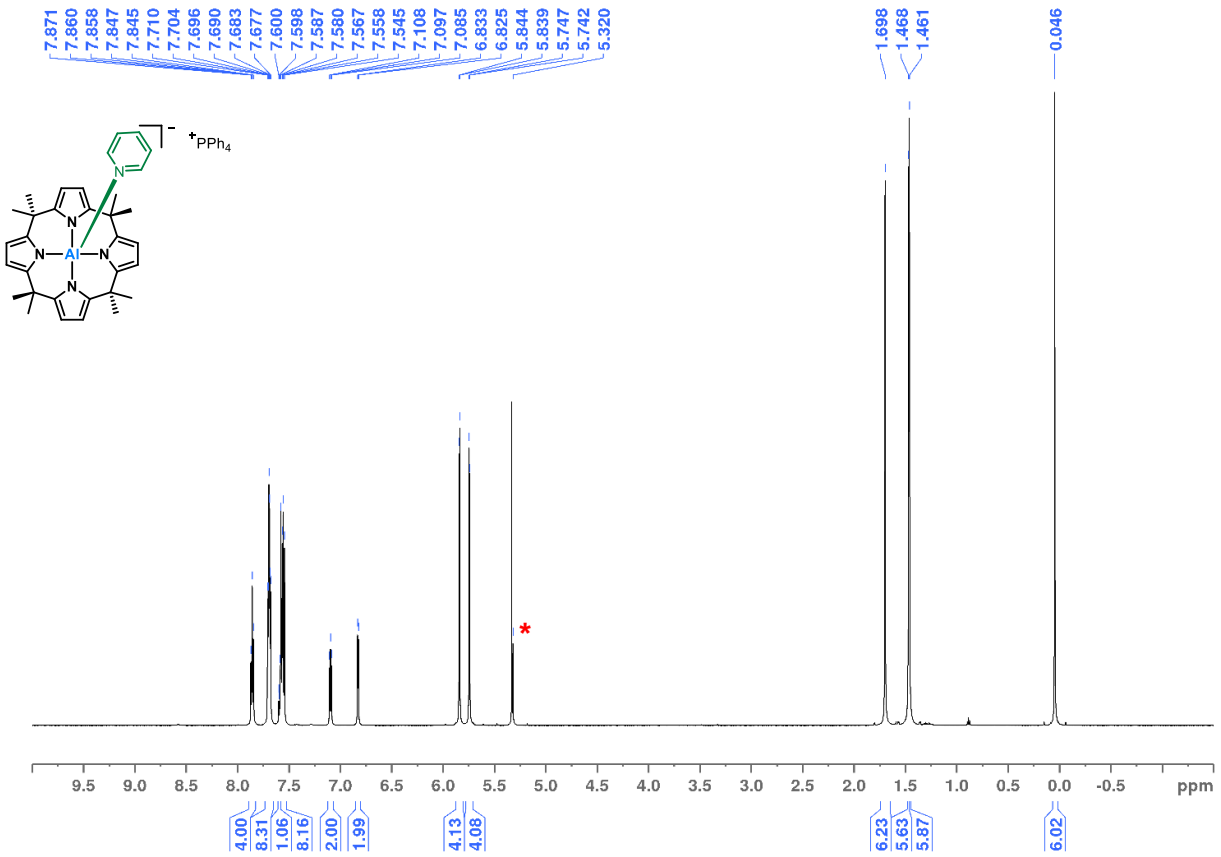


Figure S-55: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [PPh_4][(pyridine)-**1**]. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in [PPh_4][**1**], are marked with a red asterisk.

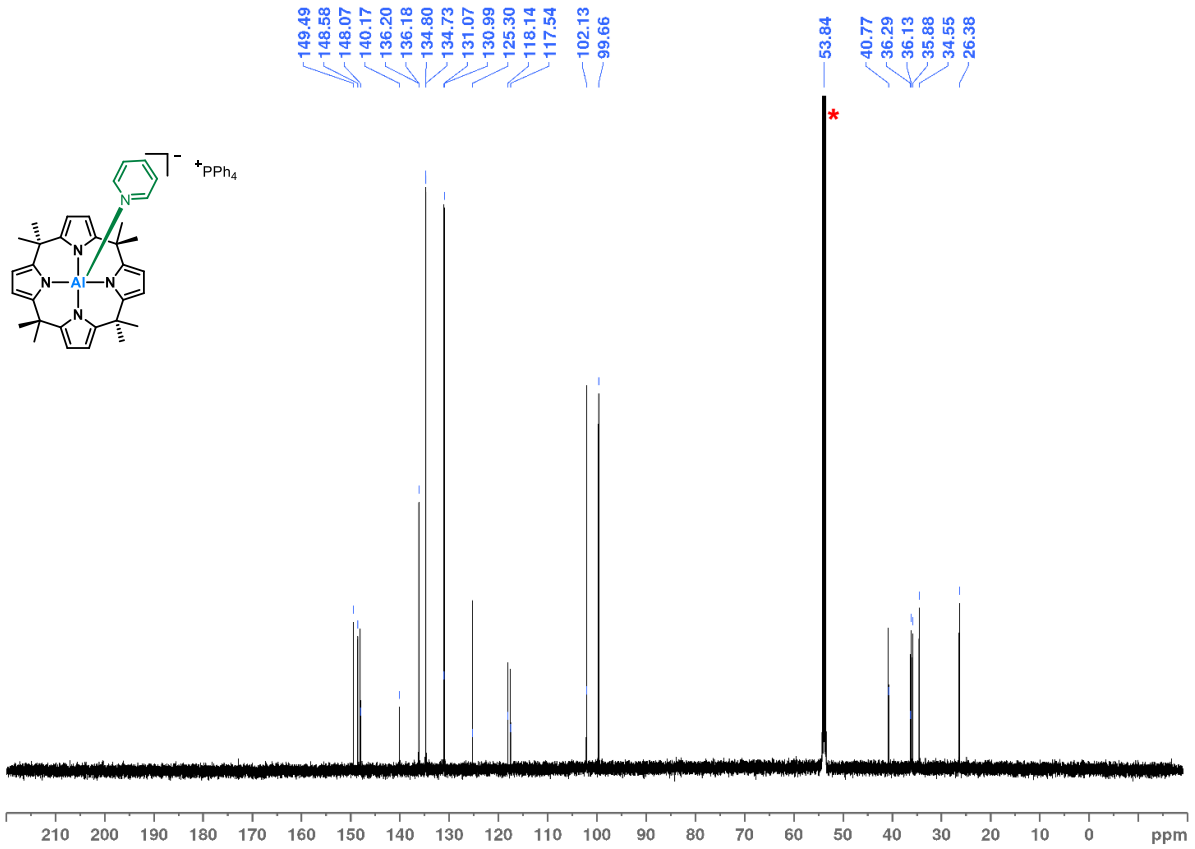


Figure S-56: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of $[PPh_4][$(pyridine)-**1**$]$. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4][$**1**$]$, are marked with a red asterisk.

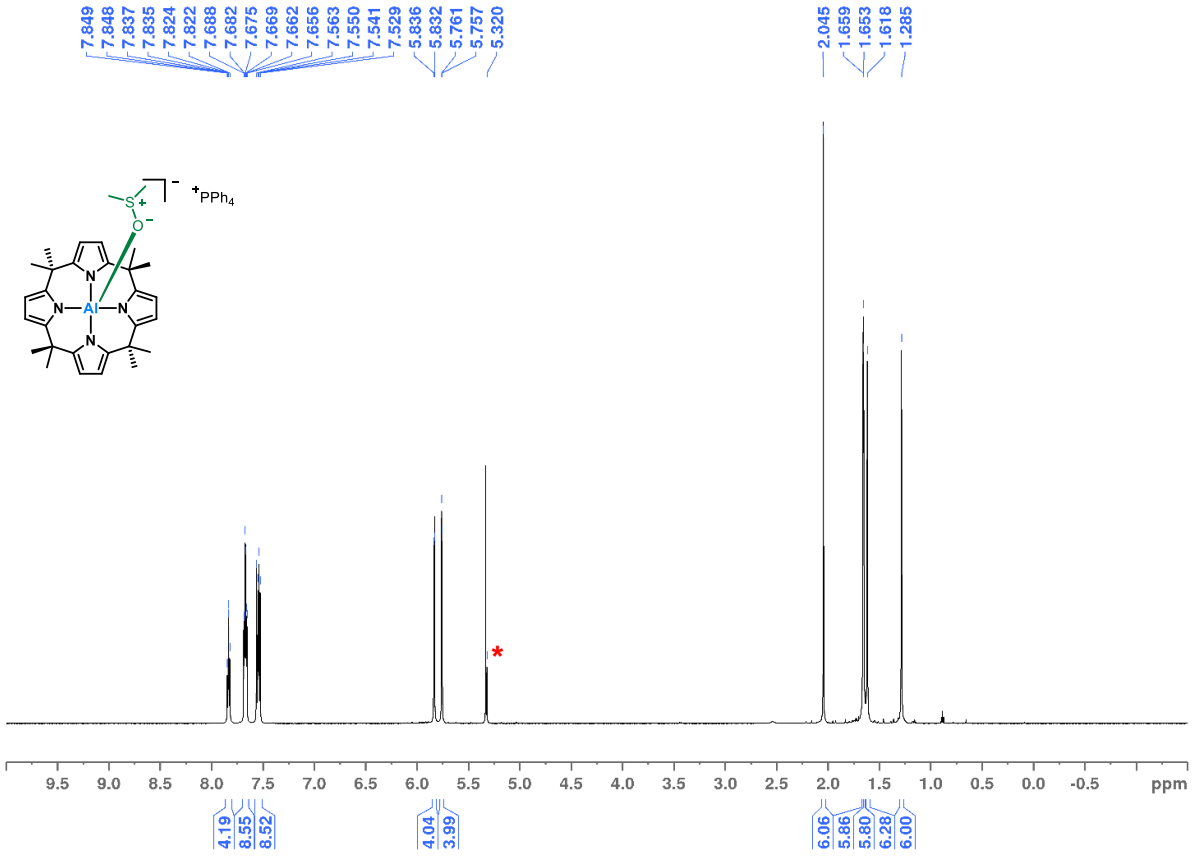


Figure S-57: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of $[PPh_4][$(dmso)-**1**$]$. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4][$**1**$]$, are marked with a red asterisk.

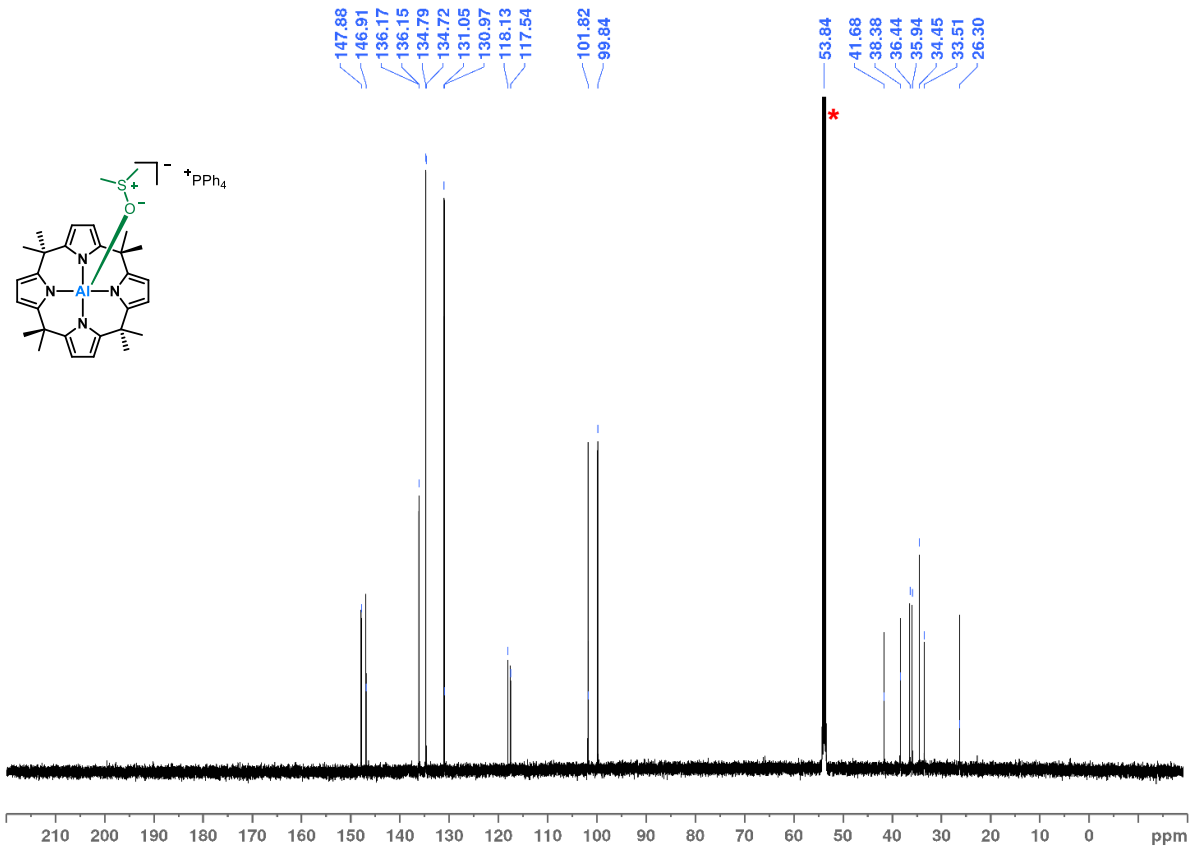


Figure S-58: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of $[PPh_4][$(pyridine)-**1**$]$. The signal of $CHDCl_2$ and that of residual CH_2Cl_2, which is contained in $[PPh_4][$**1**$]$, are marked with a red asterisk.

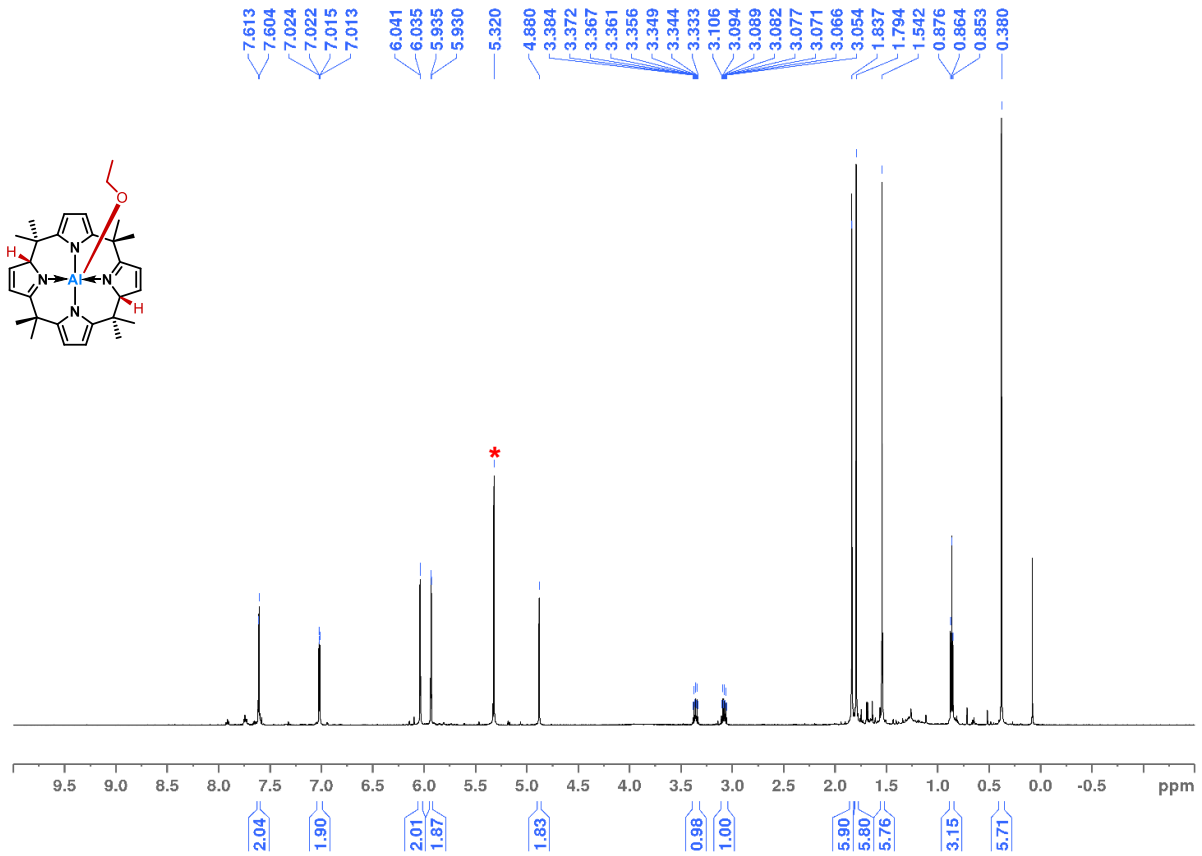


Figure S-59: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of (EtO)-**1****-HH. The signal of $CHDCl_2$ is marked with a red asterisk.

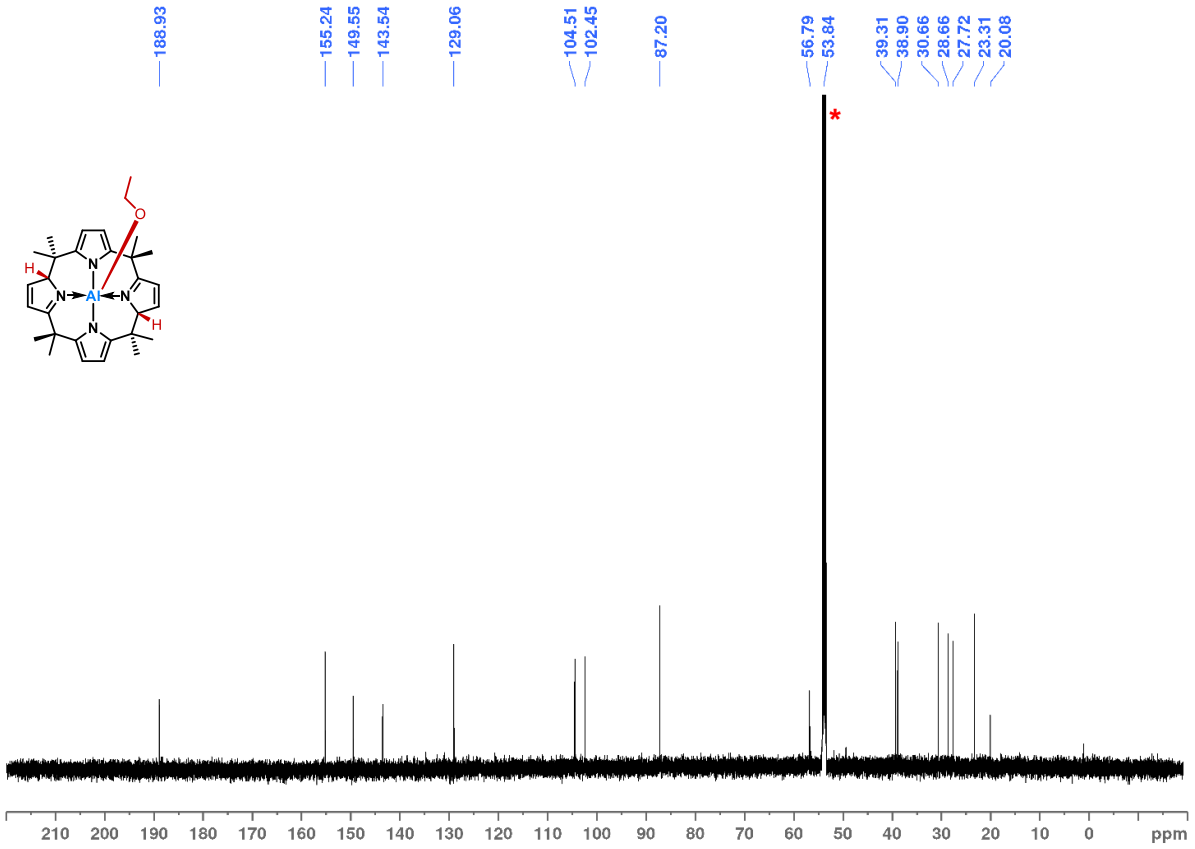


Figure S-60: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of (EtO)-**1****-HH. The signal of $CHDCl_2$ is marked with a red asterisk.

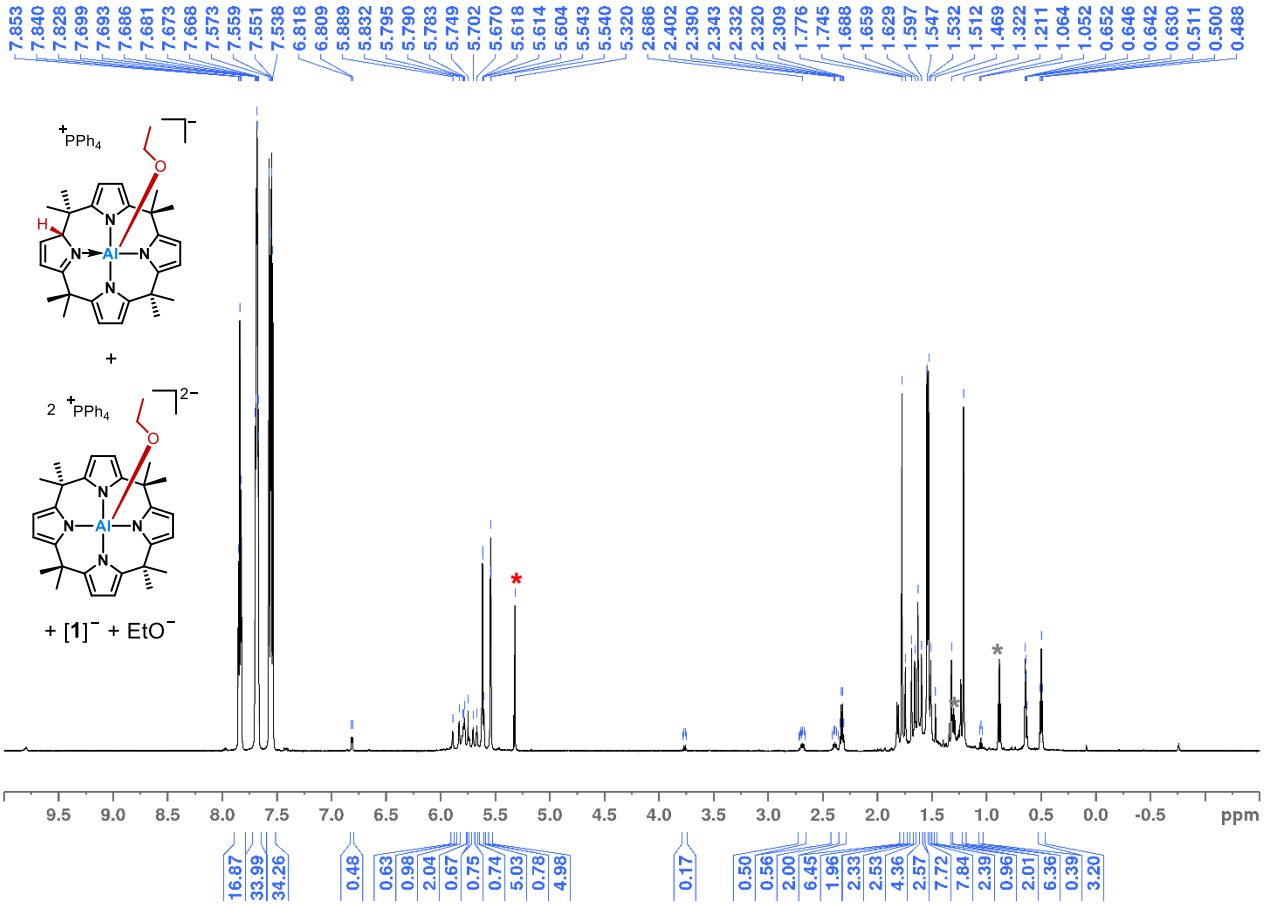


Figure S-61: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with EtOH as substrate. It is a mixture of $[PPh_4]_2$[(EtO)-**1**], $[PPh_4]$[(EtO)-**1***-H] (1:0.5), [**1**]$^-$, and EtO (1:1). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

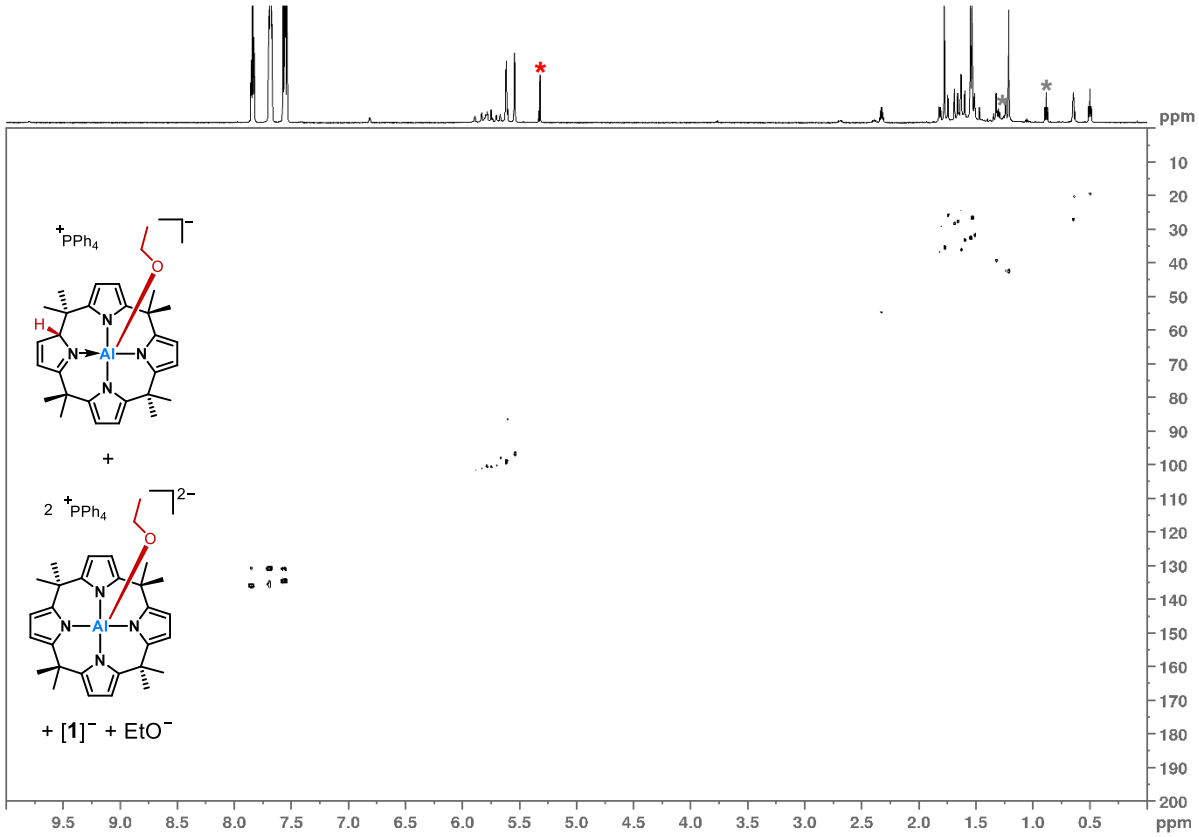


Figure S-62: $^{1}H,^{13}C$ HSQC NMR spectrum (600, 151 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with EtOH as substrate. It is a mixture of $[PPh_4]_2$[(EtO)-**1**], $[PPh_4]$[(EtO)-**1***-H] (1:0.5), [**1**]$^-$, and EtO (1:1). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

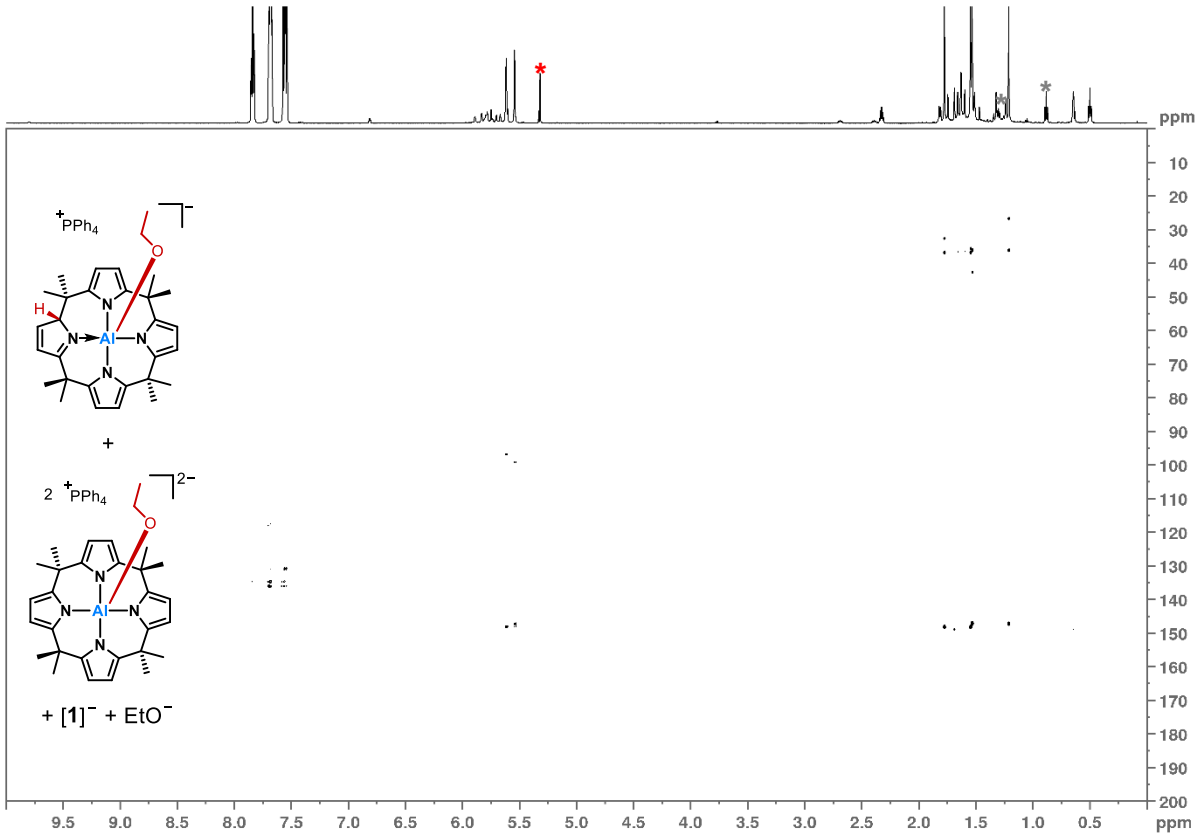


Figure S-63: $^{1}H,^{13}C$ HMBC NMR spectrum (600, 151 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with EtOH as substrate. It is a mixture of $[PPh_4]_2$[(EtO)-**1**], $[PPh_4]$[(EtO)-**1***-H] (1:0.5), [**1**]$^-$, and EtO (1:1). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

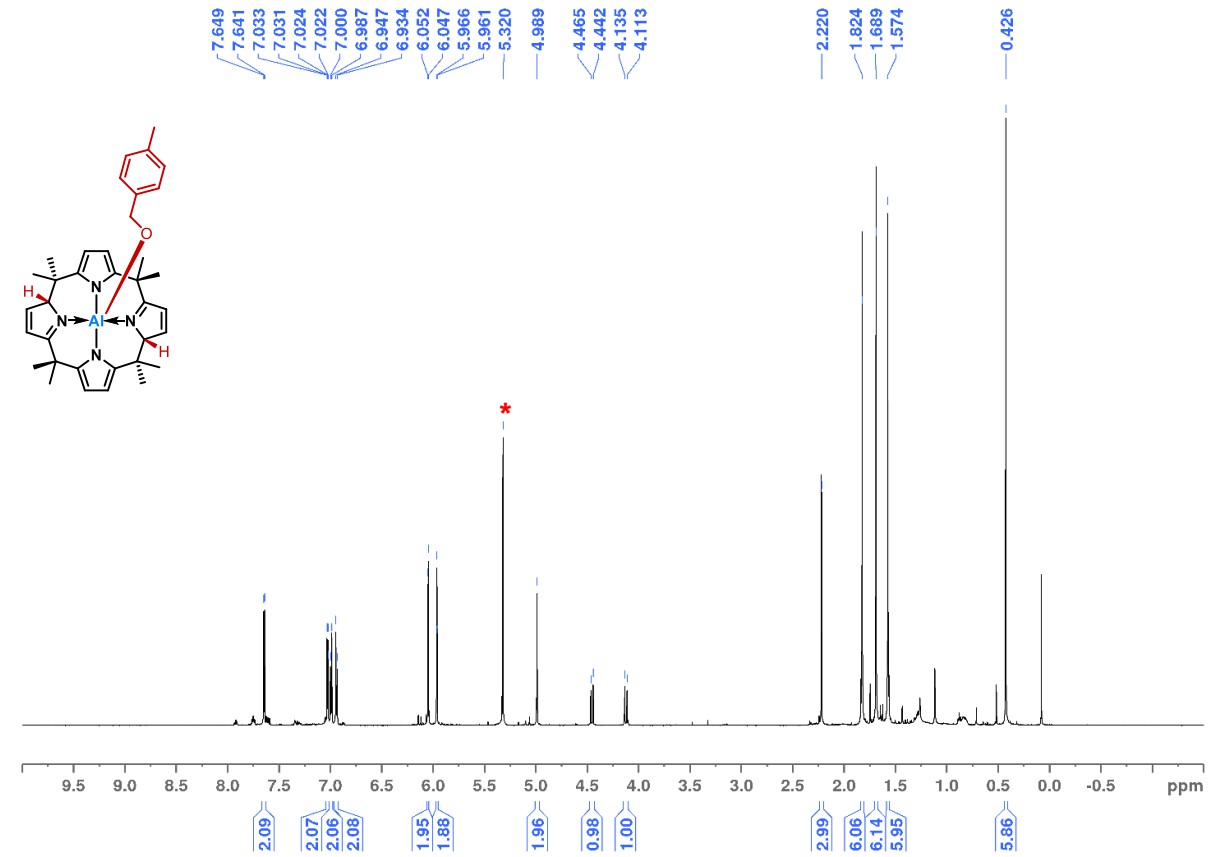


Figure S-64: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of (*p*-MeBnO)-**1****-HH. The signal of $CHDCl_2$ is marked with a red asterisk.

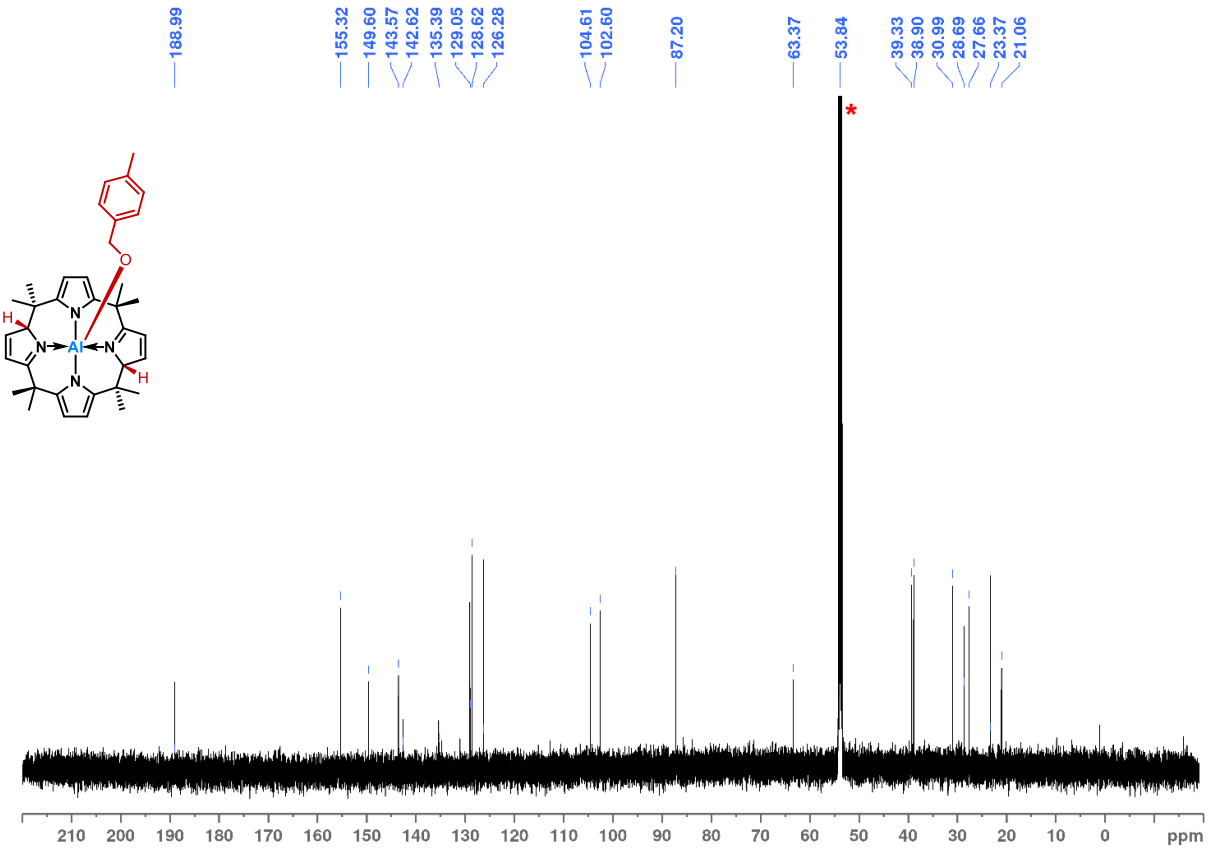


Figure S-65: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of (*p*-MeBnO)-**1****-HH. The signal of $CHDCl_2$ is marked with a red asterisk.

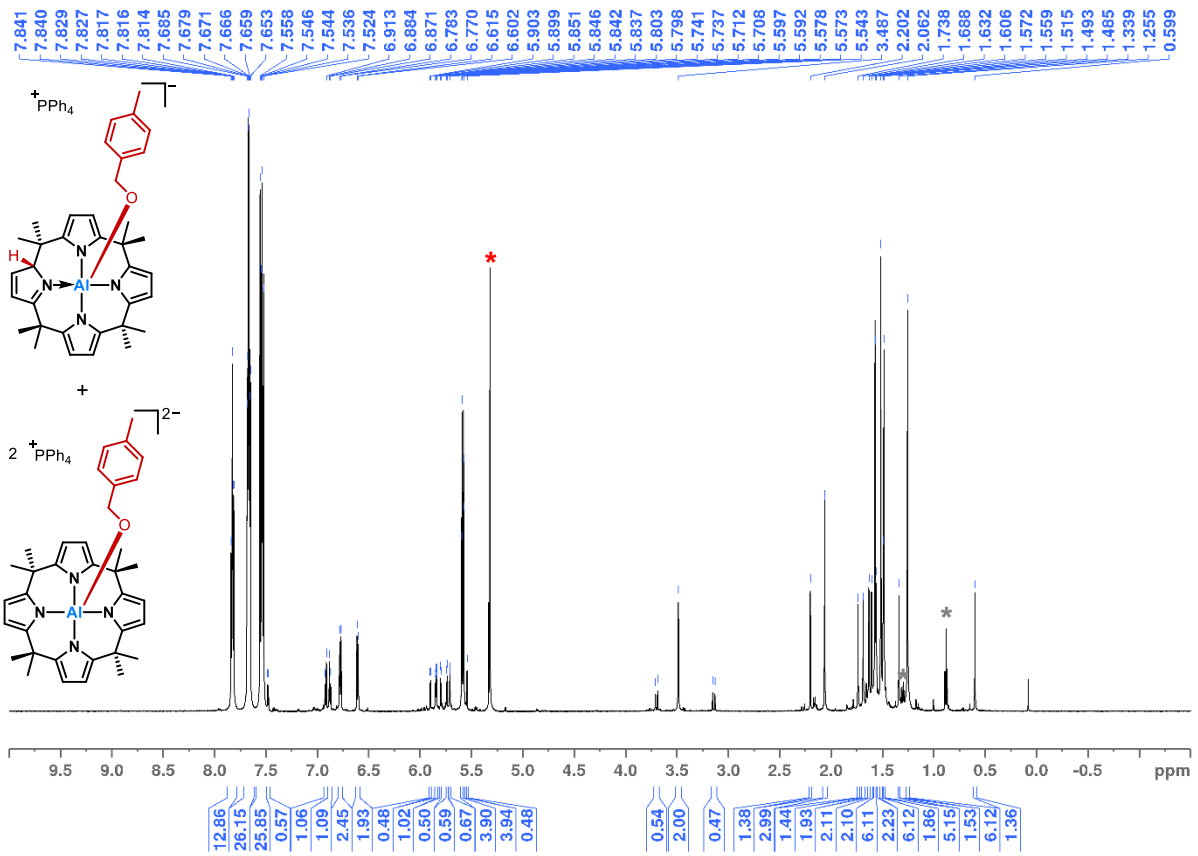


Figure S-66: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with *p*-MeBnOH as substrate. It is a mixture of $[PPh_4]_2$[(*p*-MeBnO)-**1**] and $[PPh_4]$[(*p*-MeBnO)-**1***-H] (1:0.5). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

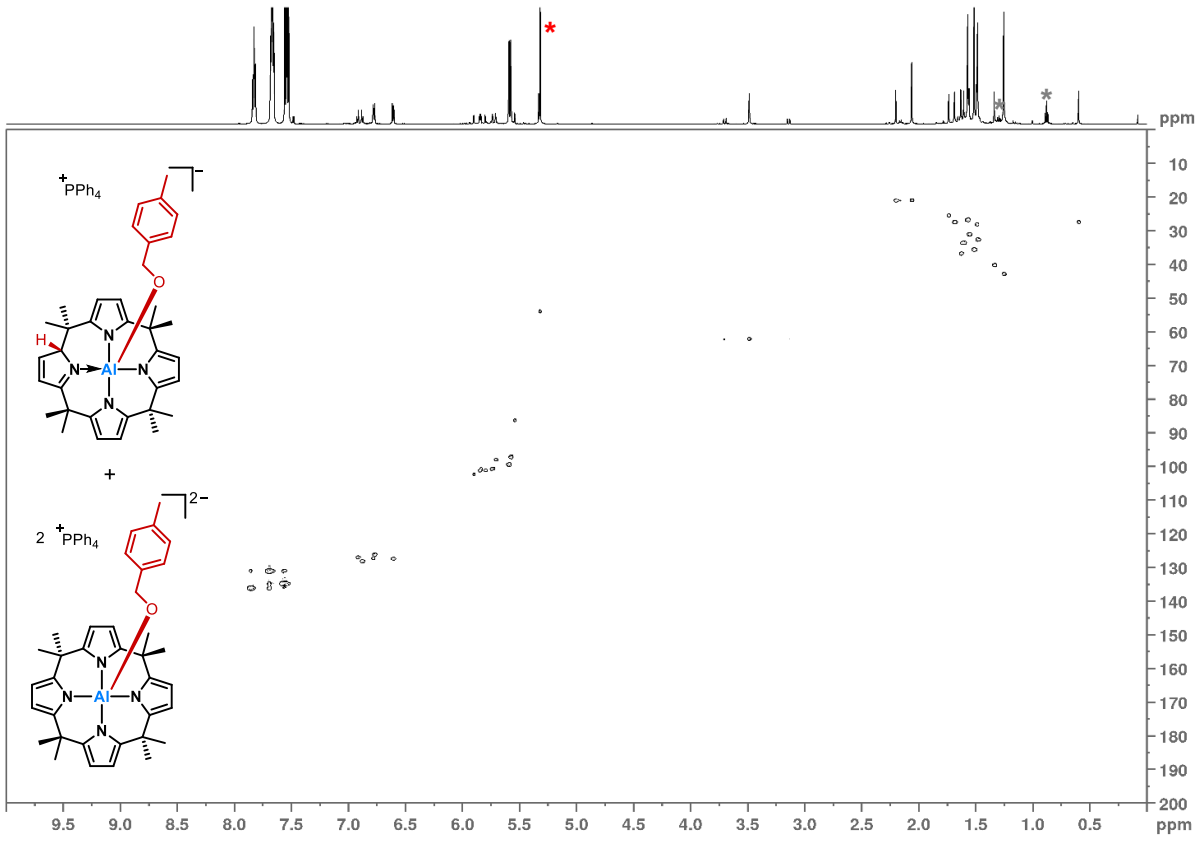


Figure S-67: ^{1}H,^{13}C HSQC NMR spectrum (600, 151 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with *p*-MeBnOH as substrate. It is a mixture of $[PPh_4]_2$[(*p*-MeBnO)-**1**] and $[PPh_4]$[(*p*-MeBnO)-**1***-H] (1:0.5). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

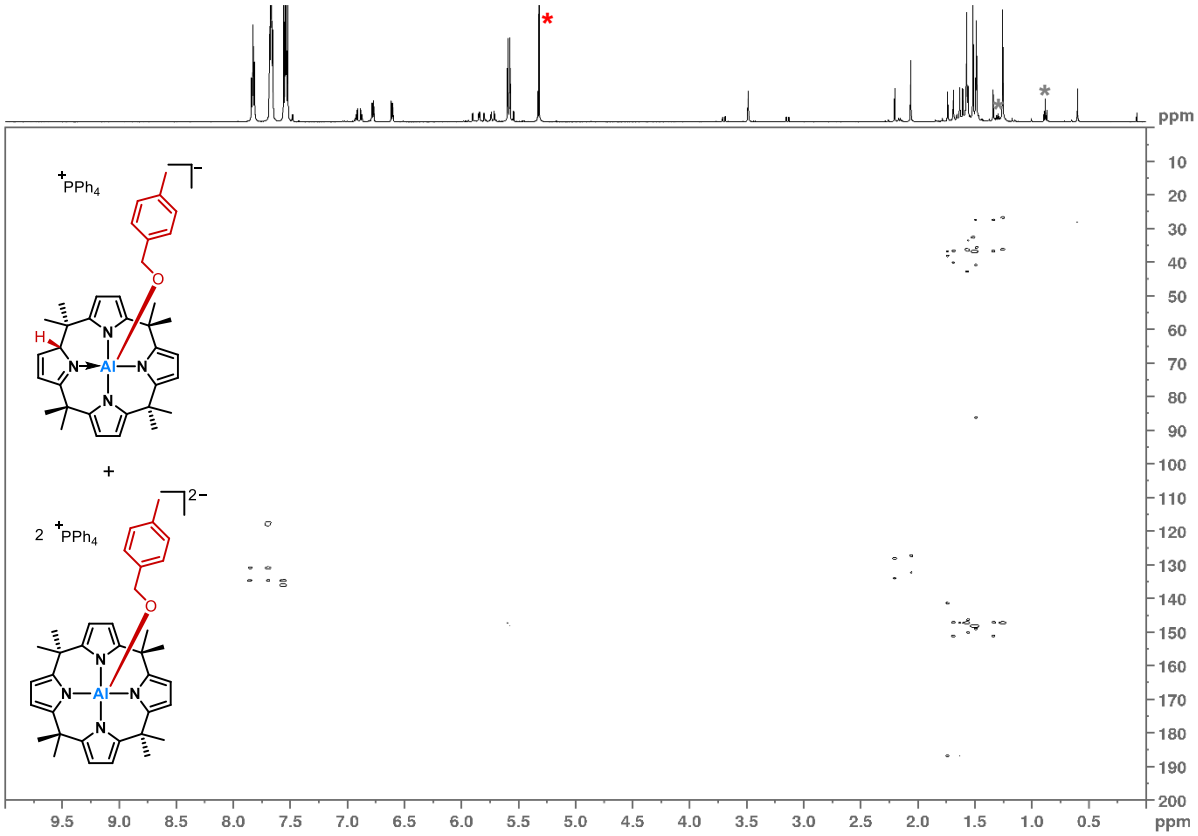


Figure S-68: $^{1}H,^{13}C$ HMBC NMR spectrum (600, 151 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with *p*-MeBnOH as substrate. It is a mixture of $[PPh_4]_2$[(*p*-MeBnO)-**1**] and $[PPh_4]$[(*p*-MeBnO)-**1***-H] (1:0.5). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

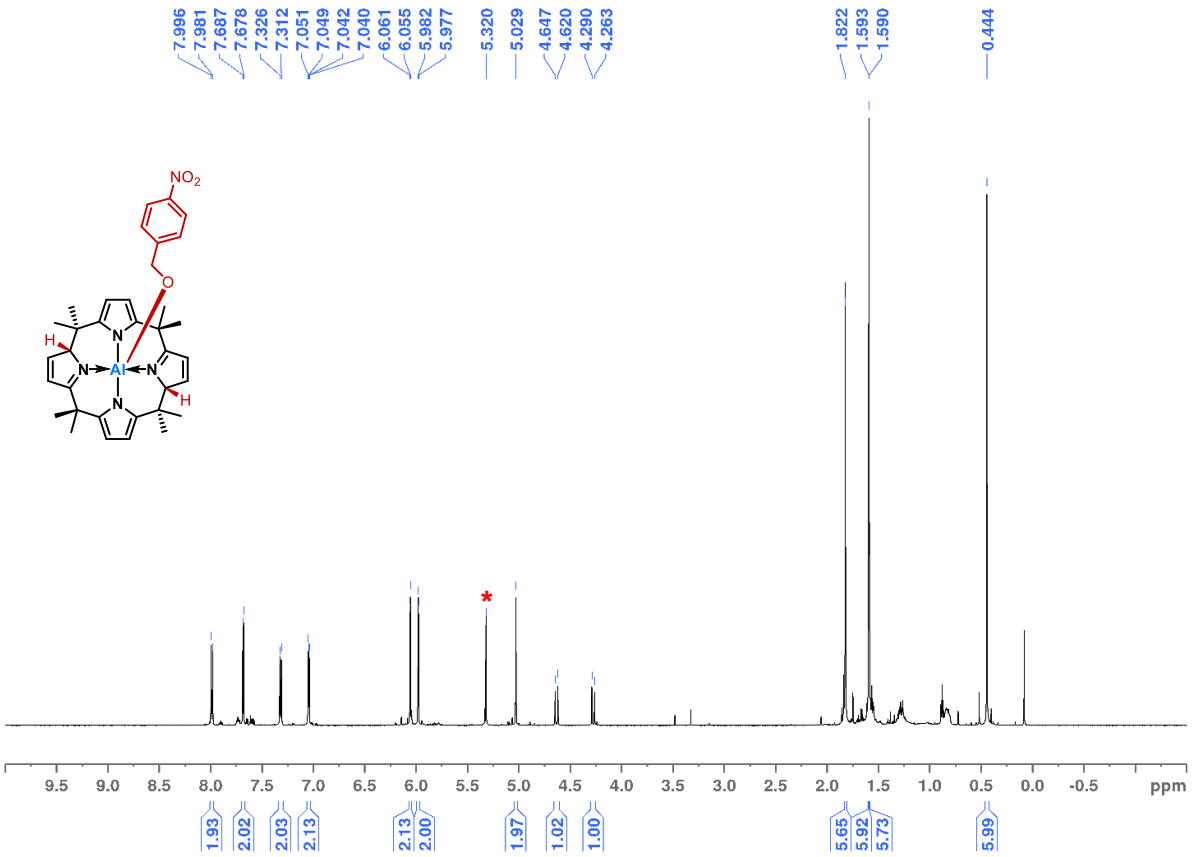


Figure S-69: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of (*p*-NO_2BnO)-**1****-HH. The signal of $CHDCl_2$ is marked with a red asterisk.

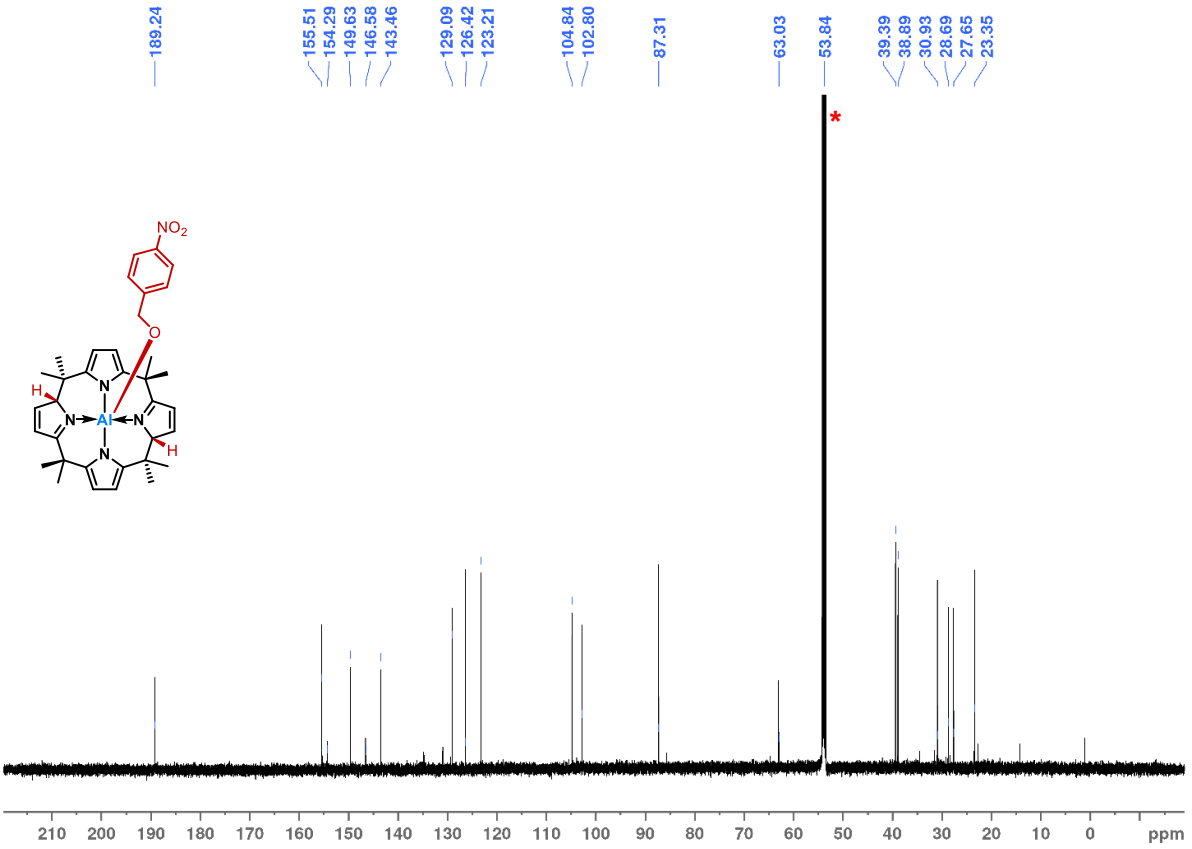


Figure S-70: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of (*p*-NO_2BnO)-**1****-HH. The signal of $CHDCl_2$ is marked with a red asterisk.

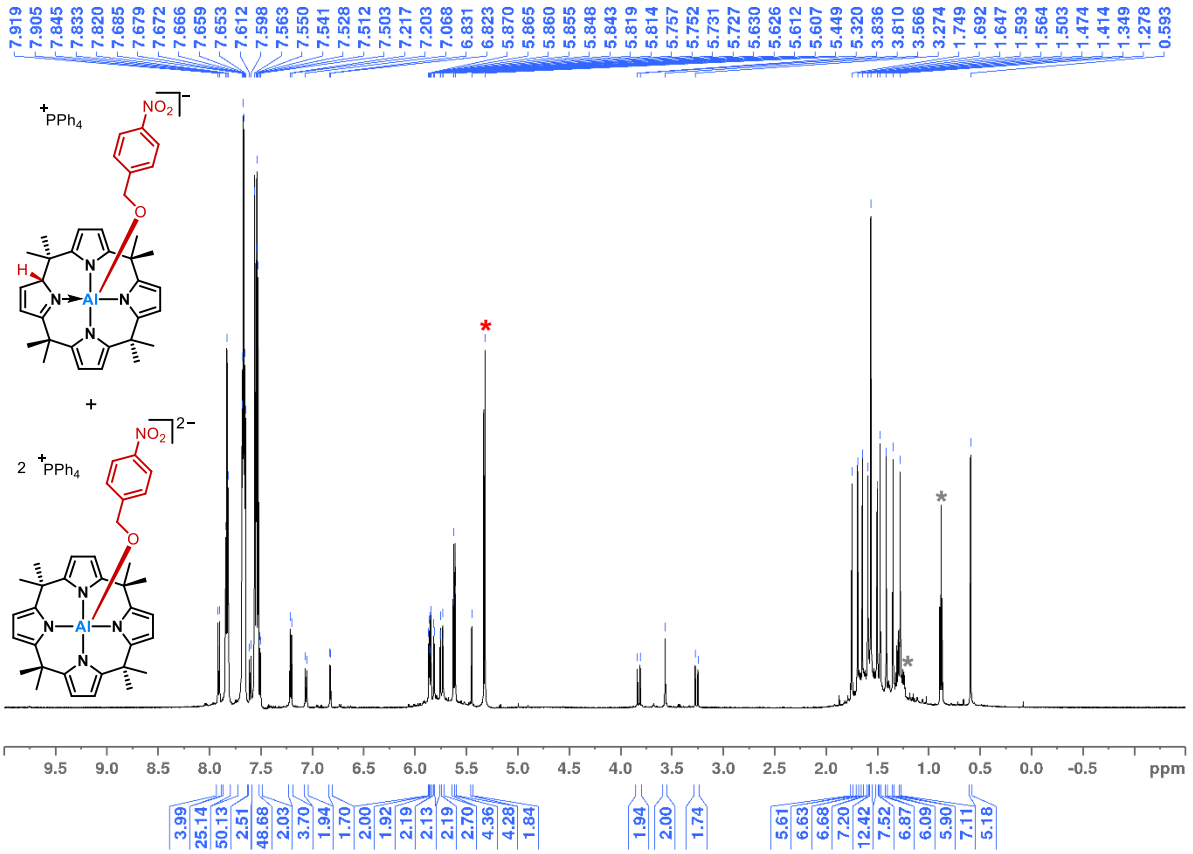


Figure S-71: ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with *p*-NO_2BnOH as substrate. It is a mixture of $[PPh_4]_2$[(*p*-NO_2BnO)-**1**] and $[PPh_4]$[(*p*-NO_2BnO)-**1***-H] (1:1.8). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

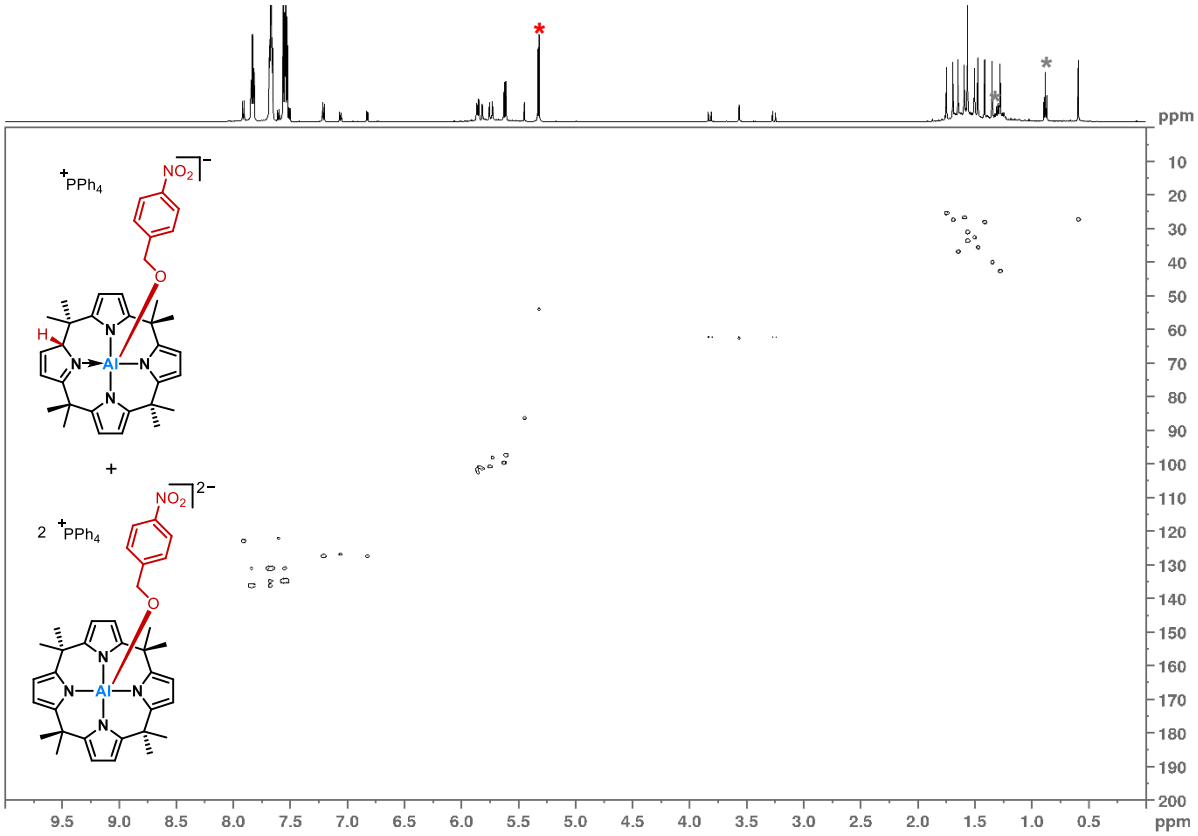


Figure S-72: $^{1}H,^{13}C$ HSQC NMR spectrum (600, 151 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with *p*-NO_2BnOH as substrate. It is a mixture of $[PPh_4]_2$[(*p*-NO_2BnO)-**1**] and $[PPh_4]$[(*p*-NO_2BnO)-**1***-H] (1:1.8). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

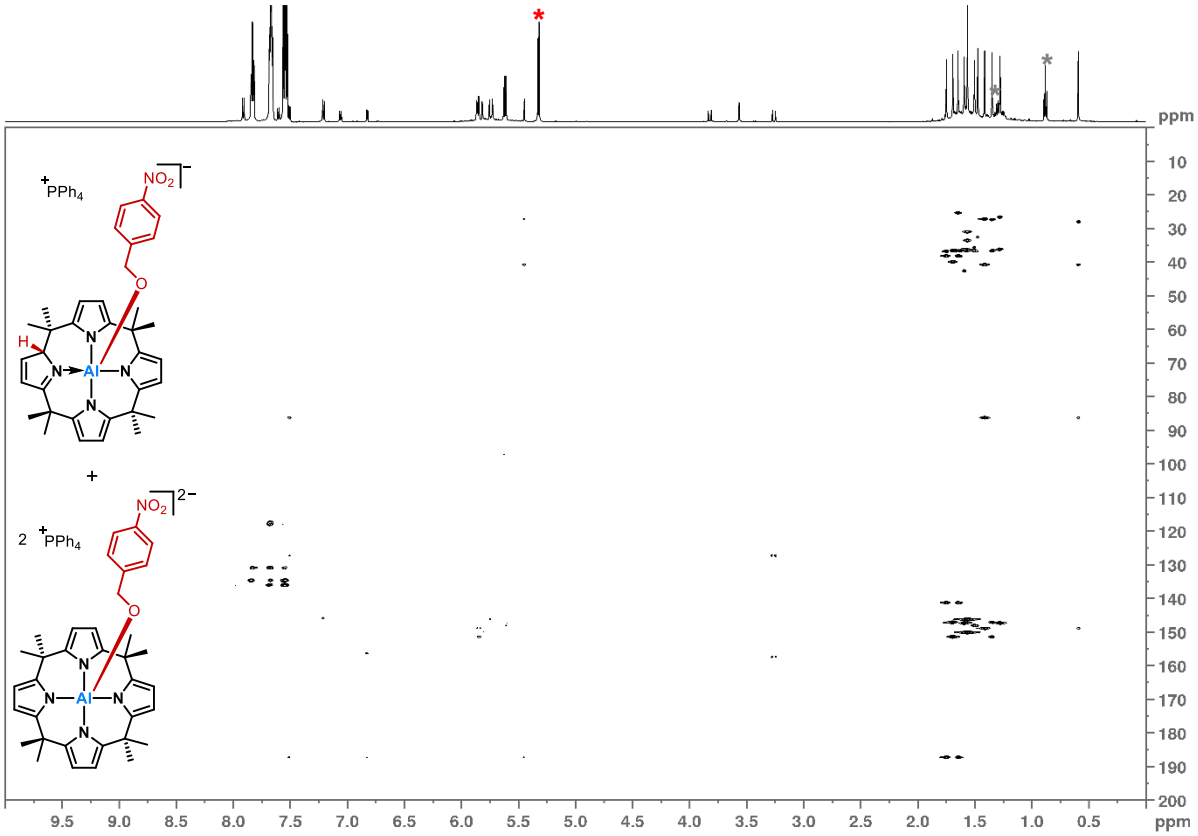
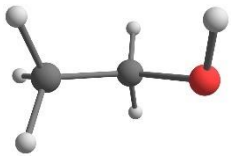


Figure S-73: $^{1}H,^{13}C$ HMBC NMR spectrum (600, 151 MHz, CD_2Cl_2, 298 K) of the solid material collected from the autoprotolysis reaction with *p*-NO_2BnOH as substrate. It is a mixture of $[PPh_4]_2$[(*p*-NO_2BnO)-**1**] and $[PPh_4]$[(*p*-NO_2BnO)-**1***-H] (1:1.8). The signal(s) of $CHDCl_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

S-18. Computed XYZ coordinates, molecular structures, and energies

EtOH

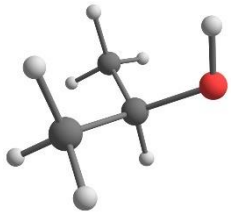


Total correction	0.08669736 E_h
Final entropy term	0.02933742 E_h
Final single point energy	-155.29838007 E_h
COSMO-RS correction (Gibbs free energy)	-14.7696 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-23.8110 kJ mol^{-1}

xyz 0 1

C	-1.24420949654196	3.52355699090039	-0.04885418028097
O	-0.16980556727868	2.61759740949911	-0.09398690449899
H	-0.17472711170963	2.10238373041652	0.71552278836320
C	-2.59915098420035	2.84677599173391	0.06758408569203
H	-1.19791054575159	4.09252241410471	-0.97887040603386
H	-1.12804682437595	4.25168269960234	0.76601789939653
H	-2.75722981676679	2.14167086151104	-0.74845266534286
H	-3.40300711041510	3.58332678399008	0.03793094806625
H	-2.69706254295995	2.30043311824189	1.00870843463867

^{i}PrOH

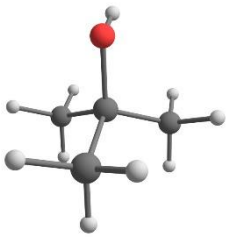


Total correction	0.11665736 E_h
Final entropy term	0.03246470 E_h
Final single point energy	-194.68487260 E_h
COSMO-RS correction (Gibbs free energy)	-17.4769 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-26.2929 kJ mol^{-1}

xyz 0 1

C	-1.27095738169071	3.41323971207307	-0.15124067566584
O	-0.23350795363106	2.46058723240960	-0.23822987446695
H	-0.20983885814816	1.96655426058148	0.58578388476638
C	-2.63456323222170	2.74998597037333	-0.00961741589770
H	-1.24301507561339	3.94261417215631	-1.10762136444384
C	-1.01904086058574	4.42105382032095	0.96236368332875
H	-2.80445198184968	2.02921863797137	-0.80930240454792
H	-3.43794395235588	3.48693205560385	-0.04428754699995
H	-2.72128087024944	2.22263268768378	0.94472205513190
H	-1.05605267961655	3.94259989566806	1.94530619513399
H	-1.77289565762583	5.20934456016045	0.95984552498622
H	-0.04142149641186	4.89024699499774	0.85275793867497

^{t}BuOH

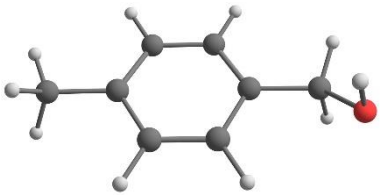


Total correction	0.14636802 E_h
Final entropy term	0.03620215 E_h
Final single point energy	-234.071173690355 E_h
COSMO-RS correction (Gibbs free energy)	-19.6007 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-28.2005 kJ mol^{-1}

xyz 0 1

C	-2.23837764131824	1.11636215204564	-1.63172068509501
C	-1.34957209611979	0.67101818151150	-0.47028172338827
H	-3.27082796080132	1.24352813504121	-1.30388926805601
H	-2.22912415405050	0.38766743145789	-2.44333868658652
H	-1.89935085528415	2.06821011446673	-2.04978778451852
C	-1.85387763999482	-0.64714678666168	0.10125938093367
H	-2.88076304614118	-0.55128424987803	0.45593640704983
H	-1.23703772115718	-0.97017483321990	0.94069936316679
H	-1.83008961398439	-1.43054470476568	-0.65654427935620
C	0.09683851568660	0.52192913097684	-0.94243482634959
H	0.18413191068900	-0.22740378910417	-1.73026808967668
H	0.74531303333395	0.22233533397423	-0.11822609155980
H	0.48192528133036	1.46161224450802	-1.34799277688306
O	-1.42596552975510	1.60465881271894	0.59364405246572
H	-1.11467248243324	2.45535282692846	0.27322500785364

p-MeBnOH



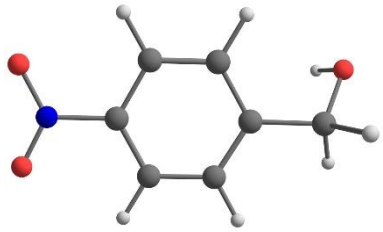
Total correction	0.17443551 E_h
Final entropy term	0.04218567 E_h
Final single point energy	-386.762174510 E_h
COSMO-RS correction (Gibbs free energy)	-27.3892 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-36.6899 kJ mol^{-1}

xyz 0 1

C	-4.78260519409441	3.28902719320226	0.28961023638515
C	-5.05789937110284	1.93094081153185	0.19654913176888
C	-3.98741367416739	1.06283581148129	-0.01114045066935
C	-2.69156233039549	1.53411447767343	-0.12473216536980
C	-2.42091549770759	2.89767409003885	-0.03381834239563
C	-3.48301808636393	3.76440815406847	0.18118119144250
H	-5.59267362610720	3.98869203792550	0.45785912398006
H	-4.17296817632632	-0.00260659391357	-0.08631767296942
H	-1.88021159167181	0.83560320054473	-0.28713876826568
H	-3.29782407979026	4.82912399631491	0.26895777650584
C	-1.01290583085413	3.41677284625756	-0.17954842211197
O	-0.04143724025859	2.58659888212190	0.40112942874190
H	-0.96555850054700	4.44321591500433	0.21133045290980
H	-0.75258609573348	3.48110070042802	-1.23901818480676
H	-0.26077824479808	2.47471390270765	1.32958747253451
C	-6.45777320305140	1.40365291606918	0.31854325214625

H	-7.17710689513757	2.20634729308873	0.47525791640148
H	-6.55080406965142	0.71064092558063	1.15609426406865
H	-6.75862829224111	0.86373343987427	-0.58054624029640

p-NO_2BnOH

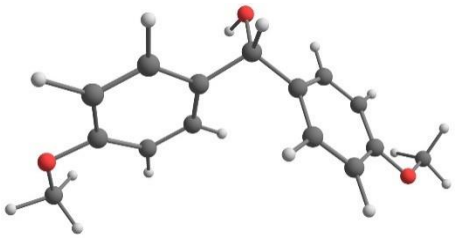


Total correction	0.15032242 E_h
Final entropy term	0.04357380 E_h
Final single point energy	-552.21078177 E_h
COSMO-RS correction (Gibbs free energy)	-38.9944 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-51.1170 kJ mol^{-1}

xyz 0 1

C	-4.87960652397382	3.28386374550873	0.29279144231691
C	-5.10804513986114	1.91875343475542	0.22626498936658
C	-4.06723197973037	1.02164815232059	0.05020482256647
C	-2.77509264490967	1.50412121268703	-0.06234330676152
C	-2.51687111519605	2.86982985234125	0.00175923613449
C	-3.58136959516141	3.74736503879535	0.18348680757055
H	-5.69896671228470	3.97278361786454	0.43562402763205
H	-4.26066964617109	-0.03976169516467	-0.00108807078816
H	-1.95909549448231	0.80857390279648	-0.20505647375999
H	-3.39593476746405	4.81293343369411	0.24631192135949
C	-1.11263325422160	3.40081233062874	-0.15026470473738
O	-0.11612658742022	2.49879310131656	0.23699399778155
H	-1.03285511674518	4.36167876571957	0.37659444276911
H	-0.93218823418670	3.61738603033978	-1.20635767268653
H	-0.19233654624814	2.34399549495599	1.18196647306870
N	-6.47387601632321	1.41618862707730	0.34840014637817
O	-7.35468891113223	2.22737001558815	0.49525615417851
O	-6.63492171448811	0.22196493877508	0.29533576761098

(p-MeOPh)$_2$CHOH



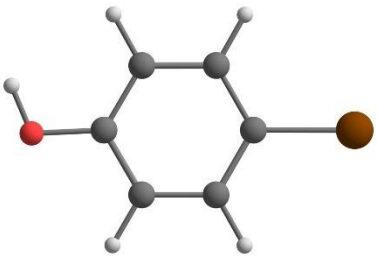
Total correction	0.30458966 E_h
Final entropy term	0.05953839 E_h
Final single point energy	-808.26457910 E_h
COSMO-RS correction (Gibbs free energy)	-52.8646 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-65.0560 kJ mol^{-1}

xyz 0 1

C	-5.69608224984290	2.17282435689113	0.15577705012575
C	-5.45673949396659	1.20086680958443	-0.80617467452579
C	-4.67351968382473	2.51441420249761	1.04308988763559
C	-3.44415884450045	1.89727697018952	0.95482114887763

C	-3.18559896927129	0.92318211416237	-0.01141452564341
C	-4.21092069749512	0.58340855521010	-0.87606015663938
H	-4.05433993714470	-0.18709786328632	-1.61873426969804
H	-6.22340394147969	0.90063741681757	-1.50750261130648
O	-6.86294106501632	2.83055264020239	0.31062051669665
H	-4.85886798493787	3.26841162133715	1.79710680188687
H	-2.66330760542777	2.18498149411779	1.64903864384811
C	-1.83352956155585	0.23861429746875	-0.05982510135916
C	-0.67985240663764	1.21775680342139	-0.06848330689539
C	-0.74104033407592	2.41502936961291	-0.76681536654457
C	0.35320481377028	3.26755697612741	-0.84675555635992
C	1.54390905010540	2.92564783544424	-0.21420483796284
C	1.61902581473394	1.72438868426049	0.49195818412162
C	0.52310855629688	0.88894986746497	0.55442610165563
H	-1.66524323906630	2.71149070263536	-1.24850788844271
H	0.25279531113776	4.19212991253752	-1.39857684654573
O	2.65846166991384	3.68085758378189	-0.22258645619424
H	2.54452212727774	1.46082833198529	0.98712875983278
H	0.60161863815055	-0.04293112477959	1.10189032508003
O	-1.72189508906673	-0.66805103037139	-1.13371269115477
H	-1.74461101160007	-0.38126307151204	0.83986469086985
H	-1.48870291341017	-0.16792430002246	-1.92115019044332
C	2.63799001741375	4.90032806963522	-0.91729827357511
C	-7.92714418663428	2.51193613867453	-0.54572355808160
H	3.62537968144162	5.34113429350348	-0.80009643152521
H	1.89656941168436	5.59633134408729	-0.51205106292402
H	2.44244962249140	4.76592341288079	-1.98598650944407
H	-8.76305603884988	3.14312944006648	-0.25209898928701
H	-8.23414673721387	1.46492301170088	-0.45509023651101
H	-7.69127272339938	2.71491513367285	-1.59555256956672

p-BrPhOH

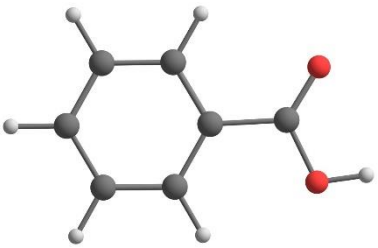


Total correction	0.10445458 E_h
Final entropy term	0.03874398 E_h
Final single point energy	-2882.7423285 E_h
COSMO-RS correction (Gibbs free energy)	-30.0285 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-38.0799 kJ mol^{-1}

xyz 0 1

C	-2.95970119022023	2.37093251238946	-0.00000004134429
C	-3.10571492596575	0.99216975503569	-0.00000005316473
C	-1.69365141571119	2.94589100130604	-0.00000004319100
C	-0.57149901792896	2.12255158162067	-0.00000005732017
C	-0.71569953206310	0.74714227164594	-0.00000001252723
C	-1.98340561331120	0.18164594603007	-0.00000001004864
H	-3.84812686833038	2.99315025206170	0.00000000636481
H	-4.09773054819403	0.56182833768076	-0.00000002890509
H	0.41536516790331	2.56588676636631	-0.00000003513636
H	0.16575325391177	0.12064727903706	0.00000003464509
Br	-2.17701950481459	-1.69263482198470	0.00000009715127
O	-1.49211148203839	4.27835011385139	0.00000004685079
H	-2.33315832323726	4.74197900495961	0.00000009662555

BzOH

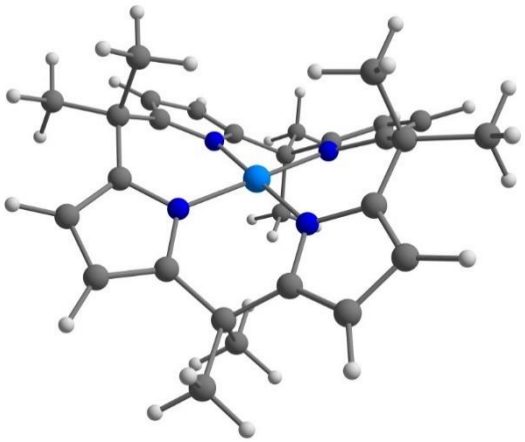


Total correction	0.12657235 E_h
Final entropy term	0.03936973 E_h
Final single point energy	-421.5474996 E_h
COSMO-RS correction (Gibbs free energy)	-28.0822 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-37.8326 kJ mol^{-1}

xyz 0 1

C	-2.15495309968916	1.10988182813458	-0.00000029907849
C	-2.30538609974371	-0.26985876770969	-0.00000053470303
C	-0.88859736090030	1.66805229231882	0.00000053716312
C	0.23737178833777	0.84890433229915	0.00000116634293
C	0.08321661905547	-0.53524704942080	0.00000086195986
C	-1.18649531333127	-1.08978383320953	0.00000007242660
H	-3.02606935916433	1.75117750352974	-0.00000075034135
H	-3.29557591735077	-0.70641456858184	-0.00000119103179
H	-0.76431320110736	2.74234016906794	0.00000074668498
H	0.94840970120292	-1.18304875925826	0.00000130486746
H	-1.30248145953260	-2.16530032340196	-0.00000011494794
C	1.56950911456427	1.50056373719816	0.00000217632819
O	1.74354052678323	2.68979975564573	-0.00000043602215
O	2.57835045824875	0.62437254541458	-0.00000087877656
H	3.40582360262708	1.12225113797336	-0.00000266087184

[**1**]$^-$



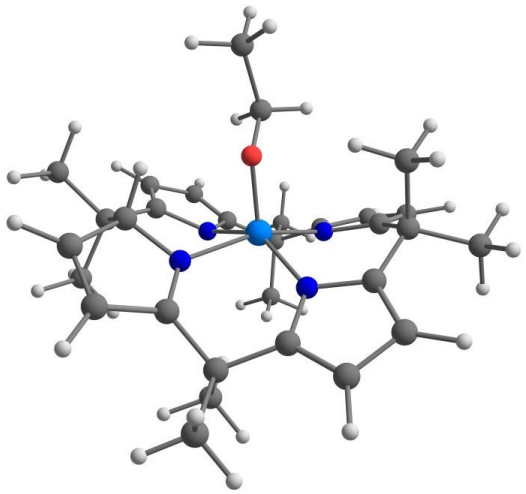
Total correction	0.58958485 E_h
Final entropy term	0.07984281 E_h
Final single point energy	-1550.4663695 E_h
COSMO-RS correction (Gibbs free energy)	-203.3389 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-219.6660 kJ mol^{-1}

xyz -1 1

N	-0.14069309726368	-2.21130694731250	0.21103413747852
C	-0.77067064112344	-3.22534334343047	0.88674957160033
C	0.38920473569872	-2.74496426275830	-0.93619244419383
C	-0.64748887514583	-4.39130807619483	0.17487883003434

H	-1.04887365089804	-5.35582429595877	0.44488132297971
C	0.10230913529700	-4.08529473948564	-0.98891977729304
H	0.39638597588530	-4.77651350083610	-1.76355767995535
N	-0.10625093353621	-0.94575481688918	2.58589995218898
C	0.45186902398218	-0.29516872965715	3.65690345573961
C	-0.73957302963569	-2.06424614706547	3.06513116925120
C	0.18073372716307	-0.99441750259412	4.80536929216199
C	-0.58922350697715	-2.12333146253593	4.42730229203533
H	-0.98676003781666	-2.87972356520506	5.08621516402986
N	0.09864627974850	1.42127674303637	1.32172475384591
C	-0.34003640880576	2.51418843725212	0.61817000686000
C	0.64084267757212	1.87581276440550	2.49698299605275
C	-0.08442343330084	3.65213237999092	1.34014471581432
H	-0.32551732653859	4.66402149254968	1.05342276847563
C	0.55088547902599	3.24385187234263	2.54007385368016
H	0.90268385019133	3.88725704563688	3.33166862962163
N	0.07003201158977	0.15542085954470	-1.05296567398275
C	0.58044410811757	-0.57442539704230	-2.09635879076599
C	-0.36746641415899	1.35258554822812	-1.56017668421272
C	0.47299039314773	0.15191128963124	-3.25490199978131
H	0.79894361016634	-0.15183727395632	-4.23762644279190
C	-0.14125493061369	1.38309056975465	-2.91275350518697
H	-0.38913072895598	2.18667809279610	-3.58884359667043
H	0.48401276608137	-2.81779442816613	-3.68240095727945
C	1.43596095186200	-2.63517671053694	-3.18449758104139
C	2.62511969807878	-1.69178337624786	-1.22368060961398
C	1.23397601898631	-1.90792349586737	-1.85734317705387
H	3.11756063636587	-2.64880749956130	-1.04087914231994
H	1.93110969345154	-3.59432181555218	-3.02677501412436
H	2.56687743353336	-1.17273703421235	-0.26408798120732
H	-2.71733328820275	-1.29799392542506	1.28749946064649
C	-2.87191329143934	-2.25204548621649	1.79700461728941
C	-1.87414385741945	-4.26190064367367	2.85364581402054
C	-1.54039718106589	-2.94913501875414	2.14921818761845
H	-0.96855078462498	-4.80256355557117	3.12764875555654
H	-3.46924280126864	-2.87732299207682	1.13055829985084
H	-2.47599598364084	-4.90388752041490	2.20892192815046
H	2.59548713804884	0.00188865442280	1.93026476797517
C	2.68022161585407	0.50732021521553	2.89515373641931
C	1.54218277596711	1.62215010484116	4.79588710429137
C	1.30516256172379	0.92741538023259	3.45720956332035
H	2.04610564262178	0.95249307420279	5.49421757798876
H	3.17942095509113	-0.18453219508785	3.57631686396034
H	0.60232439134508	1.94236839956565	5.24488784362221
C	-1.07526778252318	2.34954835076791	-0.68374337197460
C	-2.51203018921563	1.85863348170075	-0.40450044800003
C	-1.17484854047154	3.69449869176381	-1.39969080380878
H	-3.06373203592970	1.73390489236765	-1.33826516145410
H	-1.72700465268396	3.59316187218602	-2.33503701673083
H	-2.52819442691177	0.89384785916788	0.10799944243937
H	-0.18660012152452	4.09418308758231	-1.62567882020225
H	-3.04417535870543	2.56823733192343	0.23201879080240
H	-1.70693608821781	4.42080988378078	-0.78377371558894
H	3.25561638972808	-1.08573217268887	-1.87721385892147
H	2.06697655564805	-2.04838593023141	-3.85347972862754
H	-2.45153938439633	-4.07677814034612	3.76048306711532
H	-3.44765534204682	-2.04299880383076	2.70069805224796
H	2.17846431290734	2.49897428818260	4.66794953267361
H	3.31728456985523	1.38090387786040	2.74381350143175
H	0.49752823164127	-0.73856421188842	5.80460589787967
Al	-0.01919822131518	-0.39497152361218	0.76641226553798

[(EtO)-**1***-H]$^-$



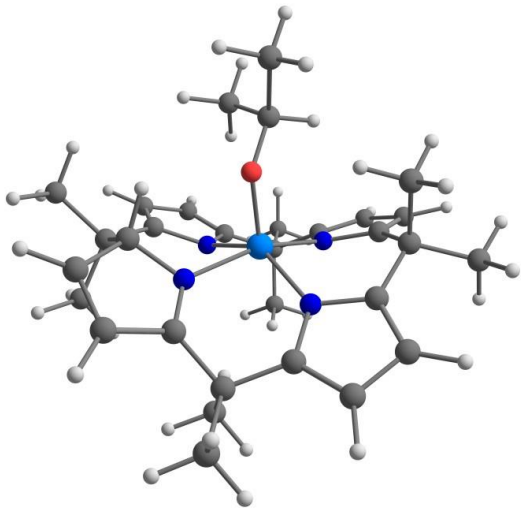
Total correction	0.67920261 E_h
Final entropy term	0.08983106 E_h
Final single point energy	-1705.796358 E_h
COSMO-RS correction (Gibbs free energy)	-217.1127 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-234.069 kJ mol^{-1}

xyz -1 1

N	1.14309229429018	-1.43959155996696	1.80145066423907
C	2.75278858169398	-1.15106001977658	3.59536803204889
C	3.27109344256274	-1.96844170517310	4.77675919794206
H	3.82228526132028	-2.84847007546474	4.43877233733727
H	2.46095406812429	-2.29208088801612	5.43091837524657
H	3.95909305782890	-1.36894334903543	5.37127186788517
C	3.95501351105155	-0.76105939886502	2.70880770784084
H	4.48240021850187	-1.64280872763036	2.33336127310122
H	4.65335656106204	-0.16303912495983	3.29467878450216
H	3.64487416125440	-0.16608038114510	1.85023057932033
N	1.24697961585287	0.83702783133521	3.24990107089727
C	0.84122085250777	1.92649372297871	3.97439581143063
C	2.02943996040065	0.07821150571351	4.07549759545575
C	1.35827922185287	1.85082377507248	5.24964947625017
H	1.20954340698673	2.55892774985014	6.04940428509684
C	2.12148425826706	0.66670899439808	5.31541968928628
H	2.67496351682149	0.30551193810635	6.16879667715524
C	-0.09406193056602	2.97852577011601	3.42677105600151
C	-1.55322397089702	2.48602934548274	3.52781810737459
H	-1.81765258123234	2.31221799083420	4.57412048464784
H	-1.70359890687901	1.55626895671786	2.98568010156472
H	-2.23205016645034	3.23826708698772	3.11911553323810
C	0.01006235597362	4.23824826282178	4.29348071368674
H	-0.67449117999608	5.00647217372491	3.93222077023409
H	1.01995955134686	4.64743387689208	4.28511063608225
H	-0.27006126491714	4.02270414323842	5.32573347275954
N	0.76265556381247	2.42606973841339	1.11055877409652
C	1.04417275402246	3.09274179477144	-0.04529411752346
C	0.27450773227258	3.33968565566629	2.00671367615698
C	0.71571735234422	4.42163550939078	0.09288336649584
H	0.83930780099225	5.19996177281158	-0.64470469573264
C	0.21999935158307	4.57863647679171	1.40700991496745
H	-0.11443188125319	5.50069001082781	1.85716799882182
C	1.79868981710820	2.41931406500410	-1.15753708079849
C	1.70148402855290	3.25786751710853	-2.43056988514464
H	2.11058319706711	4.25448165463223	-2.26151607398091
H	0.66678309539276	3.36771287313438	-2.75593850307959
H	2.27302203658278	2.80201805315253	-3.24078485364544
C	3.28811358932052	2.33387320707078	-0.76050511836512
H	3.87185324820889	1.84449354236839	-1.54427476401384
H	3.41902587396683	1.76565749728434	0.16019855726468
H	3.69299565124132	3.33359157244629	-0.59067831755940
N	1.25645790198607	0.07223473453000	-0.43921635571940
C	0.85764875967375	-1.10151181931663	-1.04570118181026
C	1.29418801347047	1.02711363769994	-1.42198275257813

C	0.62837628740327	-0.87541042906293	-2.38431391493975
H	0.32331663704605	-1.60176050563767	-3.12222777762332
C	0.91316463497828	0.48389085797330	-2.62652772927476
H	0.84563082166992	0.99500285130188	-3.57391461321447
C	0.93851408783539	-2.47014199163365	-0.41168253717243
C	0.05479725954448	-3.45842036277543	-1.17588367524672
H	0.38873995310837	-3.56008694861577	-2.20776022557168
H	-0.98420919867587	-3.12728011439197	-1.19094877268494
H	0.09385440485679	-4.45575792958600	-0.73280379159879
C	2.39828206038154	-2.94546668836462	-0.48766751060642
H	2.73060001014973	-2.90151865999392	-1.52462268761102
H	2.52548425437695	-3.97063506587057	-0.13056794249773
H	3.05950541614338	-2.29705645041617	0.08722192551075
C	1.82632719266484	-1.97164504349331	2.74748216576743
C	0.44987255374251	-2.46333426831276	1.06544527047661
H	-0.61991918235706	-2.22980261746947	1.07226849913294
C	1.60295761531888	-3.41418749257184	2.80675138205581
H	2.03372479878867	-4.08851262829005	3.53021898529144
C	0.76100317092585	-3.71271806548461	1.81129513181642
H	0.37904036642634	-4.69115258529526	1.56004143188094
Al	0.67320664667868	0.51907694599238	1.39796085799730
O	-1.04771589269855	0.11405981140869	1.33488761977508
C	-1.90725088384812	0.66117415562082	0.38846485658433
C	-3.26259949546442	-0.02740269858394	0.44632018481712
H	-1.51093001737745	0.56344342934744	-0.63403844072157
H	-2.05577679864064	1.74033805021133	0.54939550208788
H	-3.16726189869122	-1.09470794814546	0.23247030974993
H	-3.95253075182842	0.39991466731291	-0.28503229898132
H	-3.71126183556582	0.07575233680182	1.43631490632380

[(*i*PrO)-**1***-H]$^{-}$



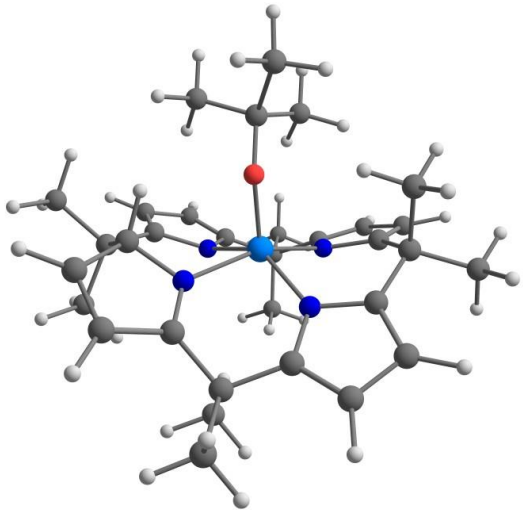
Total correction	0.70932639 E_h
Final entropy term	0.09123002 E_h
Final single point energy	-1745.183536 E_h
COSMO-RS correction (Gibbs free energy)	-213.8968 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-230.1363 kJ mol^{-1}

xyz -1 1

N	1.66593343466193	-1.62746252451883	2.15420819816577
C	3.35311305210989	-1.29946558831109	3.87007299307950
C	3.93346130587344	-2.09903319050959	5.03525083662429
H	4.47136339915421	-2.98131311763519	4.68211672421862
H	3.15801065986888	-2.41674225137394	5.73288305394096
H	4.64776816997261	-1.48994209442249	5.58733346021547
C	4.50858417132459	-0.91400542703493	2.92090253049808
H	5.02463398450145	-1.79676788714905	2.53213097262892
H	5.22966804627642	-0.30355369042274	3.46499568403691
H	4.15137404243347	-0.33279328747298	2.07122120229026
N	1.79552586490179	0.66197207695203	3.58952868650562
C	1.42819870297039	1.75975313923559	4.32281332187259

C	2.64946320294332	-0.06732296605591	4.36976678587876
C	2.04487042311333	1.72132549702907	5.55469384956186
H	1.94390866399477	2.44284506314159	6.34991678593014
C	2.82880075415712	0.55042443066222	5.58597725119656
H	3.45139828732368	0.21570536721901	6.40162058588758
C	0.40640338765592	2.76599613380631	3.84912182638453
C	-1.00666497777800	2.21535363833225	4.12622614043753
H	-1.16005692755104	2.10469071946710	5.20262403055839
H	-1.14698284137533	1.23944117545875	3.67180514223605
H	-1.76674306733370	2.89475259826775	3.73360503904277
C	0.55122714907512	4.05330717470550	4.66922212311337
H	-0.20030261594702	4.78404505835631	4.36826592289819
H	1.53588927094059	4.50091255115788	4.53832769685091
H	0.39561359333580	3.85712924399794	5.73112173284718
N	1.11442332812875	2.21372136938109	1.48181906729245
C	1.28858367528969	2.87689622349167	0.30291956643154
C	0.61317463728222	3.10648293374673	2.39095869946253
C	0.86142410032528	4.17840133131742	0.43652448495073
H	0.89130428124697	4.95138895989159	-0.31617307906328
C	0.42604845497240	4.32389383964027	1.77287628549881
H	0.05232317311990	5.22890657535761	2.22682477026032
C	2.08902718955855	2.25919704996324	-0.81008389880006
C	1.91964416943381	3.08215348496496	-2.08585353528016
H	2.23583272198356	4.11210177235642	-1.91788707012330
H	0.88043223021071	3.09542142478863	-2.41536934207812
H	2.53351834391873	2.68023012888426	-2.89338724610714
C	3.58117877569324	2.30361636685094	-0.41388747420054
H	4.20312162726910	1.86550927936389	-1.19856506563677
H	3.76039905425612	1.74937204506920	0.50728771230524
H	3.89922881825543	3.33442225625500	-0.24473513811301
N	1.67939698976486	-0.11757777859899	-0.07780251906006
C	1.39312712202046	-1.32111456812294	-0.68898270039441
C	1.70911192792869	0.82744900765229	-1.07094809929580
C	1.23479315209510	-1.12640125499559	-2.04253163038882
H	1.01717423167903	-1.87888598676992	-2.78513741992793
C	1.44046764047422	0.24485112969230	-2.28792574651389
H	1.39442411059736	0.73886768404731	-3.24550367275977
C	1.47606634518955	-2.68502382786932	-0.04184775915854
C	0.58874784158920	-3.67883613478802	-0.79678924913424
H	0.92312946128379	-3.79704294018288	-1.82658769097909
H	-0.44773102805131	-3.34060269174558	-0.81897844568426
H	0.62035616968272	-4.67070809546150	-0.34042049865537
C	2.93520222519828	-3.16273409317440	-0.12095902354809
H	3.26490541746303	-3.11523985431648	-1.15842037809987
H	3.06283492811550	-4.18910911896768	0.23210124111127
H	3.59981686862646	-2.51769131723495	0.45404932527541
C	2.39682500395502	-2.13879944621426	3.07602693019857
C	0.98632435421397	-2.67218341583747	1.43669924494332
H	-0.08782084054964	-2.46284488290822	1.44469938268061
C	2.20419145918234	-3.58521201548968	3.15252789862589
H	2.67204709741040	-4.24548878765775	3.86576315657880
C	1.33822902433743	-3.90846492015498	2.18598060243821
H	0.97173477298867	-4.89672679371271	1.95068765712275
Al	1.11087049016692	0.30790571341612	1.77251960386844
O	-0.58796549778463	-0.17932056615905	1.81972877219704
C	-1.70737298484257	0.39266209126875	1.22600110491600
H	-1.70673948464107	1.48761574910168	1.35402809488985
C	-2.96240726317703	-0.14853260288556	1.90921852464893
C	-1.77419044176509	0.11847574238100	-0.27437686348258
H	-2.94850816809685	0.05636897488963	2.98059037070325
H	-3.03260763438656	-1.23175028732994	1.77770442215706
H	-3.86700860147003	0.30011295788406	1.49221818269757
H	-0.91974518014149	0.54111847837067	-0.80168075514338
H	-2.67971176681688	0.55302006530677	-0.70672957849308
H	-1.78773145978793	-0.95609309763823	-0.47507379803385

[(*t*BuO)-**1***-H]$^-$



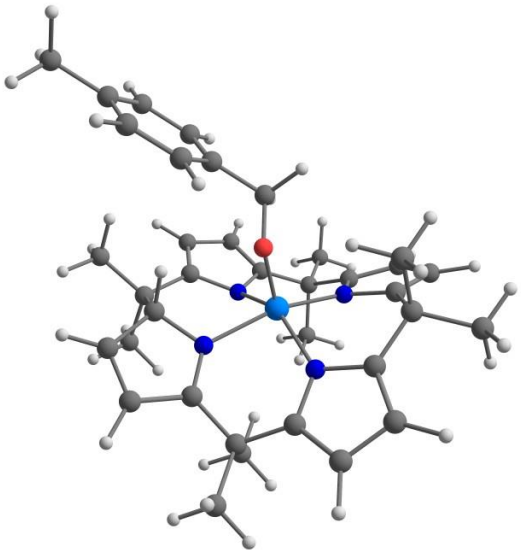
Total correction	0.73923982 E_h
Final entropy term	0.09315268 E_h
Final single point energy	-1784.566758 E_h
COSMO-RS correction (Gibbs free energy)	-212.5899 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-228.1245 kJ mol^{-1}

xyz -1 1

N	1.63541619537215	-1.59612563670706	2.13250036741389
C	3.31428256580491	-1.34623598961056	3.86940621132466
C	3.87379952555135	-2.18857702998503	5.01454841722339
H	4.39620993865287	-3.07085885568322	4.63899042127141
H	3.08961321520715	-2.51038451275392	5.70045455390647
H	4.59771050010433	-1.60914964668813	5.58548575553723
C	4.48313622560116	-0.95363715358019	2.93934667257355
H	4.98809724722844	-1.83306795971695	2.52911404927735
H	5.20949521695931	-0.37094946007654	3.50632974020751
H	4.14100915326744	-0.34154769954595	2.10532412803292
N	1.80103449088800	0.65847011164810	3.63288137560401
C	1.48469454658146	1.75622044404831	4.39056647556071
C	2.63211913481288	-0.11544388317067	4.39674640958217
C	2.10137606134041	1.66958685806602	5.61944665502468
H	2.03323027541550	2.38022334241382	6.42768643087043
C	2.83865641825663	0.46956454077151	5.62429749072756
H	3.45320018566705	0.09596756500802	6.42896304280612
C	0.52234234861873	2.82557486136621	3.93896261672945
C	-0.91877920799405	2.34975361984780	4.20321295052369
H	-1.07177630172153	2.19651093054030	5.27431022744069
H	-1.12004515211262	1.40948919454059	3.69983593115467
H	-1.63941771297241	3.09253566415099	3.85189821555320
C	0.73713816336220	4.08600689739146	4.78557585105350
H	0.02986545488199	4.86418414412818	4.49696306219793
H	1.74623630935773	4.47938842787128	4.66709810678593
H	0.56544809949550	3.87835531516042	5.84281761202674
N	1.22116615239560	2.29182580913898	1.56064841657439
C	1.39550636759444	2.97241956423586	0.39147989180952
C	0.75007038614544	3.18286816054113	2.48878386480652
C	1.00350104343773	4.28143284374599	0.55104100437547
H	1.04250448592782	5.06562706476172	-0.18938339313598
C	0.58785729876832	4.41495186162454	1.89446286322430
H	0.24233774953843	5.32098714763860	2.36820455144258
C	2.13373257293494	2.34945276009581	-0.75843789256946
C	1.95377375896570	3.20549528067888	-2.01095626221769
H	2.30744506230422	4.22100322508366	-1.83082078364055
H	0.90641644767573	3.25830181531413	-2.30954373259597
H	2.53148390527241	2.80353175496362	-2.84453546468296
C	3.63906934672261	2.32884586264576	-0.41185048907648
H	4.21782981366680	1.88358976289636	-1.22495825859729
H	3.82458181236825	1.74873708177678	0.49184058800145
H	4.00166955967043	3.34328878071023	-0.23340596308956
N	1.67218060869806	-0.03120523002400	-0.06530074359455
C	1.41018934424039	-1.22432469654670	-0.70747508791845

C	1.69988066284101	0.93599152421306	-1.03847305281376
C	1.25236704872313	-1.00049883150804	-2.05664114800342
H	1.04505491594038	-1.73811115588020	-2.81676804258221
C	1.43780528837190	0.37918440159836	-2.26868367986520
H	1.39611124905926	0.89318413000579	-3.21579900186877
C	1.49620233533748	-2.59993371977447	-0.08884538937999
C	0.65039184092458	-3.59427324172799	-0.88960567360467
H	1.01387854836181	-3.67783804531440	-1.91287925088477
H	-0.39357229900289	-3.28295068568624	-0.93028798186424
H	0.69718468113970	-4.59629833087916	-0.45787528818637
C	2.96407421518563	-3.05457316760904	-0.13754489956977
H	3.31602276263744	-2.98934996968943	-1.16676112004101
H	3.09825266534509	-4.08366622079730	0.20471234533888
H	3.60652853664186	-2.40771254336424	0.45938437056970
C	2.34970583010154	-2.14395406699447	3.04692115238310
C	0.96312123502661	-2.61760389266950	1.37457756591199
H	-0.10922903187190	-2.40607234074896	1.35814215378519
C	2.13852130559221	-3.58935495892192	3.08494222008524
H	2.58835558239051	-4.27258788220694	3.78798770993019
C	1.28405799211077	-3.87719984541095	2.09834568314986
H	0.90809756498174	-4.85370363772112	1.83148139964528
Al	1.10382618405131	0.37468231449479	1.79638628003699
O	-0.60847116019519	-0.04790266228014	1.84626389255898
C	-1.78946680315499	0.22154810849664	1.15796910729811
C	-1.86545981649676	1.66594943866209	0.65251690034261
C	-2.96608186233047	-0.04511014749476	2.10801091297076
C	-1.93951533744490	-0.71103011711291	-0.05210621339097
H	-2.95042582042889	0.63589870841706	2.95951964707067
H	-2.91854827974075	-1.06482184369048	2.49679909743997
H	-3.92536259914365	0.07873621566570	1.59952628656510
H	-1.12534083089045	-0.57185326285642	-0.76366198423450
H	-2.88065055314427	-0.52444361143060	-0.57602486276818
H	-1.94630269668134	-1.76014777667844	0.25978097613618
H	-1.73300106109340	2.38631375186099	1.45960546442031
H	-2.83382262518660	1.85932533914147	0.18268458162512
H	-1.09187828191143	1.86736508717604	-0.08949603773160

[(*p*-MeBnO)-**1***-H]$^{-}$



Total correction	0.76592243 E_h
Final entropy term	0.09619874 E_h
Final single point energy	-1937.2667471 E_h
COSMO-RS correction (Gibbs free energy)	-220.9848 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-236.9148 kJ mol^{-1}

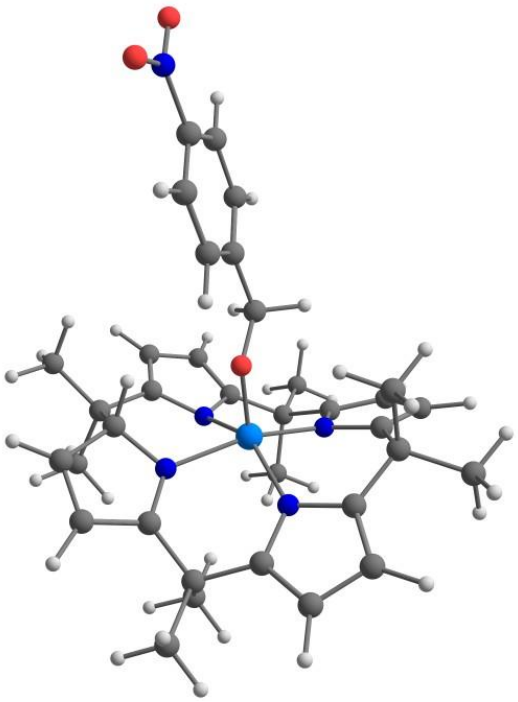
xyz -1 1

N	1.05786280267762	-1.44741990082085	1.80780073098121
C	2.69602548425990	-1.16013742604220	3.57702376402683
C	3.22267188729040	-1.97341689168257	4.75769908146236

H	3.76171238854661	-2.86049501057089	4.41888501636992
H	2.41832990381722	-2.28581007026341	5.42438998429928
H	3.92325838924914	-1.37566489228317	5.33917382754335
C	3.89065631925344	-0.78721032164811	2.67327124269797
H	4.40467511894061	-1.67663972598822	2.29773549702544
H	4.60185699781790	-0.19161325984612	3.24601486753930
H	3.57671138554801	-0.19540906383753	1.81391033595724
N	1.21668883721934	0.84721961123501	3.23253279870520
C	0.83083116104116	1.94649980578934	3.95379725753355
C	1.98964385457014	0.07836743037256	4.05820724176195
C	1.34841801183597	1.86499511171763	5.22829724174802
H	1.21442277865526	2.57863645510801	6.02569173211468
C	2.09232051935259	0.66873023470757	5.29610322770066
H	2.64239052047504	0.30168114772210	6.14913020952612
C	-0.07330487540549	3.02245093321441	3.39885119175842
C	-1.54894457827088	2.58267022799955	3.50277806929155
H	-1.81813922042063	2.41866666979636	4.54940190649606
H	-1.73430965071371	1.66001732939285	2.95978378795539
H	-2.19986921322076	3.35997230337238	3.09564122168641
C	0.07281952837529	4.28415885966179	4.25669426303668
H	-0.58716664340058	5.07173375613881	3.89140338102833
H	1.09547794596151	4.66016098665129	4.24510730977505
H	-0.21287418506194	4.08444263701336	5.29052269496076
N	0.73672346060478	2.42043442313096	1.07711154832534
C	1.03903026909423	3.07051675687258	-0.08341163402773
C	0.30617503295778	3.36023885689970	1.97631269621701
C	0.78150535512774	4.41477132769385	0.05568819315150
H	0.93550225208231	5.18435823673707	-0.68529332888115
C	0.31026316987153	4.59925360020544	1.37481557529631
H	0.02763390381951	5.53775863169882	1.82624977887370
C	1.74004175884602	2.35967466649345	-1.20670819414458
C	1.63981989314294	3.18790020785765	-2.48645653428202
H	2.08798006160247	4.17104730158347	-2.33982458731707
H	0.60170833919634	3.33163339611496	-2.78688728011467
H	2.17386752091441	2.70352012463776	-3.30563725739748
C	3.23539019593098	2.22347598618284	-0.84783370134103
H	3.77994304102481	1.70330266915412	-1.63986906693271
H	3.36961192622218	1.66188919551804	0.07649221671858
H	3.68094469153935	3.20946807300197	-0.70153307675793
N	1.13952806821748	0.03898101984077	-0.44988415710580
C	0.69613439539224	-1.13042269691188	-1.03538443348211
C	1.17915286059596	0.98445259148251	-1.44284198198806
C	0.43677003865323	-0.90900758941746	-2.36855944610515
H	0.08915339541604	-1.63366617449744	-3.08873551931143
C	0.74932422128818	0.44093690399899	-2.63116451836766
H	0.67633430301735	0.94367577649695	-3.58275583620667
C	0.76896001473870	-2.49678372707237	-0.39509168789023
C	-0.16510651514237	-3.47095469891833	-1.11651391414129
H	0.12483499356422	-3.58450312844776	-2.16058073000359
H	-1.19869443785955	-3.12408488135922	-1.08868712359253
H	-0.12194826079612	-4.46668027408034	-0.66984947129645
C	2.21655662700641	-2.99895565582947	-0.51811775108234
H	2.51487883486154	-2.96787478397384	-1.56583720579945
H	2.33498996704655	-4.02468097226879	-0.15953238109504
H	2.90936328297827	-2.36106508133401	0.03140841281164
C	1.75150366480942	-1.97892154850480	2.74752962937527
C	0.33665199987211	-2.47118988038802	1.09801794863127
H	-0.73354075007987	-2.24372821351521	1.13430314607097
C	1.51699381797182	-3.41816261989152	2.82279920464817
H	1.95403546465234	-4.08997711180039	3.54478644898510
C	0.65471964837667	-3.71703564824699	1.84485641539571
H	0.25632022265114	-4.69238807772551	1.60810984534929
Al	0.61866798214087	0.51800378506359	1.39580473789068
O	-1.11857704007351	0.16167698941951	1.39404738193249
C	-1.96442382801774	0.52001848132177	0.35996270699249
C	-2.79241096162677	-0.65572292699392	-0.10554062633430
H	-1.43985652598554	0.93193363893398	-0.51487474998918
H	-2.65778073554392	1.31521078398297	0.68377158925312
C	-3.04603876438653	-0.87610250456037	-1.45297551021337
C	-3.31839968411112	-1.56336634424722	0.81191612686810
C	-3.80811461528079	-1.95846685861335	-1.87259170102354
C	-4.33541610741096	-2.86314771805641	-0.95900229095424
C	-4.07273715895570	-2.64697037391109	0.39209313921771
H	-3.11474424624486	-1.42185133300375	1.86630786072137
H	-4.46326547460998	-3.34126429227815	1.12892664394029
H	-3.97613985059595	-2.11142503873293	-2.93312518915574
C	-5.16836880559909	-4.03096418962991	-1.40557317723047
H	-2.60629512730626	-0.21086580943270	-2.18628108589955
H	-5.06437702260383	-4.21029928762645	-2.47586378365939

H	-6.22984676957430	-3.86605631230360	-1.20625183941720
H	-4.88450424781632	-4.94963627566047	-0.88968164710667

[(*p*-NO_2BnO)-**1***-H]$^-$



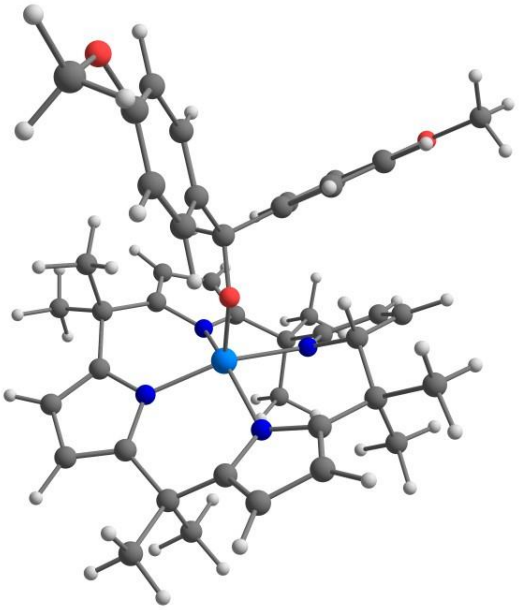
Total correction	0.74280906 E_h
Final entropy term	0.10064236 E_h
Final single point energy	-2102.7256941 E_h
COSMO-RS correction (Gibbs free energy)	-216.1824 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-233.9988 kJ mol^{-1}

xyz -1 1

N	1.37551469920970	-1.62860884417057	1.70742698186229
C	2.79175315927286	-1.12826572054013	3.61738617282130
C	3.31733107252798	-1.87017593922075	4.84480594113689
H	4.00261049737356	-2.67133311466552	4.56084452288162
H	2.50724334587987	-2.29558863396891	5.43783042317875
H	3.87298593799341	-1.18569450112450	5.48412671067098
C	3.99997421793453	-0.58476744069338	2.82467740907557
H	4.66557991957009	-1.39005021940479	2.50133349158487
H	4.56573751104231	0.09830249599997	3.45847338941233
H	3.68716659829022	-0.03382855542493	1.93803814134602
N	1.07318621050578	0.64645972014831	3.13319381826920
C	0.46655634019655	1.67055937793388	3.81319868728797
C	1.87710508168892	-0.00633310871464	4.02699790354851
C	0.88048954646156	1.65737323223831	5.12714407013506
H	0.57309561359547	2.33538492831320	5.90725199551307
C	1.78478962526185	0.58417461456712	5.26519127792143
H	2.30664252119489	0.29583204938548	6.16476242287337
C	-0.55102846339522	2.59317283647999	3.18386078629145
C	-1.94067537439476	1.92223807698665	3.18338262067880
H	-2.25834756426342	1.71414883998465	4.20803945463270
H	-1.93509463188182	0.98239460057455	2.63847099358095
H	-2.67666598283564	2.58370736579792	2.72069445832893
C	-0.67004847509204	3.85906110788046	4.03999158081327
H	-1.41833077373540	4.53346117214988	3.62252279902520
H	0.27820128945757	4.39247242007161	4.09815927014998
H	-0.99429293582142	3.61416628728983	5.05242107398105
N	0.54641991430546	2.15481053179705	0.94340494554322
C	0.81511832420952	2.85092954756127	-0.19884072123244
C	-0.12987594789481	2.99428154629375	1.78950938422721
C	0.29231468295835	4.11952862476072	-0.10395860457158
H	0.35860349577947	4.90469794026040	-0.84149596559368

C	-0.31530311271053	4.20974304524088	1.16862742903122
H	-0.80824861687769	5.07689488986166	1.58020847427473
C	1.72956180035976	2.28276685436395	-1.24700102256819
C	1.61265337363296	3.09712728318243	-2.53390051678848
H	1.87729664707726	4.13876805463613	-2.34989066467698
H	0.59756643895006	3.07230867421226	-2.93086381942389
H	2.29220393560945	2.71558963716126	-3.29763834292743
C	3.18597754898795	2.39363144589632	-0.74824301685694
H	3.88107682224164	1.98329400715316	-1.48489951293847
H	3.32765690364731	1.85036803828662	0.18581708771368
H	3.44394552804524	3.43822601606957	-0.56361200149124
N	1.46528012068543	-0.11390152300165	-0.53862035007320
C	1.25135082274530	-1.33102898177056	-1.15571916589823
C	1.42622318962316	0.83693994172222	-1.52694288768036
C	1.05309479312784	-1.13729813996172	-2.50390395259315
H	0.88008996355780	-1.89781298299086	-3.24974161165372
C	1.17041071566061	0.24759078306172	-2.74257704180525
H	1.08445847304419	0.74393752042932	-3.69625527371403
C	1.49136557156591	-2.67233356256652	-0.50710781233586
C	0.82984647280967	-3.78201145110801	-1.32667066615053
H	1.25244134416672	-3.82674399877108	-2.32961082418398
H	-0.24411223348293	-3.61797264544699	-1.42213869294486
H	0.99036397698234	-4.76264767537448	-0.87455189606599
C	3.00779017751440	-2.91767199871264	-0.46576853958347
H	3.40623214307853	-2.83176241198971	-1.47650271244583
H	3.26209977030043	-3.90842923417624	-0.08132311050945
H	3.51767249346869	-2.17096112879697	0.14286232962441
C	2.05159942546858	-2.06435027748374	2.70819672651286
C	0.89284271302968	-2.73866104330369	0.92788244024357
H	-0.19616026067291	-2.66797120691163	0.84265896666247
C	2.02640055079990	-3.52340375136205	2.76152301169727
H	2.48888306539911	-4.13285021029328	3.52181854356949
C	1.31530068355013	-3.93394830377163	1.70593700179566
H	1.09195289862828	-4.95480255986571	1.43381770852438
Al	0.71429714796408	0.25811079205390	1.25194829072853
O	-0.94778104282013	-0.35231721961014	1.04893496038484
C	-1.73692312328903	0.06041819910411	0.00080926010311
C	-2.98159888331893	-0.77631837016231	-0.12834325708594
H	-1.21680438839791	0.01954956142255	-0.97094287895520
H	-2.06216000482445	1.11047957399163	0.10849096714699
C	-3.81337105219329	-0.62351203817207	-1.23884977100189
C	-3.33957706081811	-1.70588823280399	0.84384248274121
C	-4.96455550929455	-1.36927814909304	-1.38512860279396
C	-5.29605027967986	-2.29252053140033	-0.40001891422877
C	-4.49007156752977	-2.46421587134328	0.71557563785909
H	-2.70450996507164	-1.82524779799280	1.71031097778203
H	-4.75788315755320	-3.18093624071285	1.47823432272284
H	-5.59473024678184	-1.24181835934909	-2.25292709869870
H	-3.54288309086462	0.09175830994058	-2.00662055316655
N	-6.50063684858455	-3.08846941286260	-0.54369622721832
O	-6.75763317908008	-3.89297402995720	0.32268188927918
O	-7.18688134327176	-2.90798452521827	-1.52409320531298

[(*p*-MeOPh)$_2$CHO)-**1***-H]$^-$



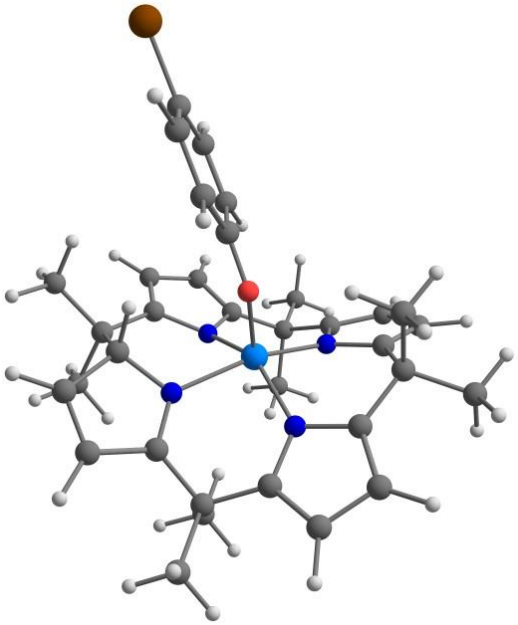
Total correction	0.89725008 E_h
Final entropy term	0.11370265 E_h
Final single point energy	-2358.765970 E_h
COSMO-RS correction (Gibbs free energy)	-239.3819 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-258.5725 kJ mol^{-1}

xyz -1 1

N	0.86540645646017	-1.22488862652050	0.68141497826127
C	1.18345954438030	-1.49804138478193	3.07235666395651
C	0.79672450498196	-2.51392411976135	4.14436022228396
H	1.31214164537601	-3.46403752938091	3.99192669368695
H	-0.27777084188052	-2.70206277901559	4.15554279369224
H	1.08126632375027	-2.14341406863703	5.12850126954137
C	2.71431929700244	-1.32166410355106	3.09508300984876
H	3.22717836982617	-2.26466195355306	2.88746932139182
H	3.02401571086486	-0.96835222644481	4.07902941786369
H	3.04716191904668	-0.58891546227752	2.36120530410405
N	0.64049560894863	0.87036673349821	2.45661095401451
C	0.02012247654225	1.94785324201017	3.03685067235562
C	0.49705756700685	-0.18285563230425	3.31486793498377
C	-0.55807637202995	1.55443813947343	4.22777508922438
H	-1.10260877162650	2.17982195423591	4.91755582289796
C	-0.24662761675816	0.19201798774838	4.41073321609558
H	-0.50909914477499	-0.41977354321131	5.26039795235612
C	0.09693096065132	3.36481783169976	2.50338857034879
C	-1.14807025970638	3.79073765244606	1.69857106845235
H	-2.07343189509580	3.52933196470622	2.21821992293659
H	-1.16339631162674	3.34603444482297	0.70818052959284
H	-1.13096960123957	4.87253918298936	1.55241042133643
C	0.17649973588691	4.30620609493439	3.71549318697119
H	0.24848389175730	5.34517336106965	3.39326879529150
H	1.03792901684310	4.07676362772520	4.34138236752121
H	-0.72390279169461	4.22826363117997	4.32609170965838
N	1.76540566522975	2.64317816405442	0.73222126124110
C	2.81153110032243	3.22251515192984	0.06749397825440
C	1.31431478776814	3.56784791139223	1.64299175754355
C	3.02028496725757	4.49779199854673	0.53666128807681
H	3.78316264204271	5.18910466025591	0.21331057088389
C	2.06132776709033	4.71832992397022	1.54490249481060
H	1.93394924687528	5.62300808181881	2.11849909195833
C	3.69060415222323	2.46267759767720	-0.88055521879248
C	4.34126463155351	3.42959864045714	-1.87073240407104
H	4.91865953483579	4.18976921591773	-1.34494270410932
H	3.59206968808529	3.93515604252837	-2.47995075939346
H	5.02983440205503	2.90217149207104	-2.53286465595049
C	4.81940075146735	1.78651281553718	-0.06915029650028
H	5.48170213884491	1.21560530168656	-0.72474788799601
H	4.40909690217333	1.10081508476888	0.67232612750021

H	5.40728755395971	2.53789142443987	0.46182220595916
N	2.25909073362206	0.40540073942494	-0.96918726189283
C	1.98423074570074	-0.57044385065616	-1.90758975202726
C	2.96101133127232	1.38496417479507	-1.62746739938194
C	2.44686980386925	-0.17560947872854	-3.13971140114254
H	2.39073048674147	-0.73300269288740	-4.06215583550800
C	3.07513541391802	1.07441603574478	-2.96044890497026
H	3.57696310416889	1.65405201433634	-3.71891609633914
C	1.56130113336447	-1.97278922514511	-1.55852177382229
C	1.01074943239209	-2.68632964192448	-2.79438336407918
H	1.76648264222922	-2.74074529657729	-3.57703377547210
H	0.14412597420615	-2.16366882998142	-3.20117209794845
H	0.71937014865527	-3.71338652901289	-2.56650815194896
C	2.79361545790881	-2.73560558160353	-1.04770521892879
H	3.57074594698504	-2.71549012771017	-1.81183098567707
H	2.56764871923725	-3.77961589473529	-0.81523729741732
H	3.20746393133079	-2.26630580015807	-0.15542207617040
C	0.79274047924445	-1.98893744631979	1.71065212573394
C	0.45313711164903	-1.96615554693786	-0.48634236125808
H	-0.41849907224159	-1.46906723612374	-0.91884964380782
C	0.29751377308782	-3.31484257318971	1.36015896006682
H	0.11262727805479	-4.12116509104593	2.05184999875588
C	0.07499870103717	-3.30217249044995	0.04327559421330
H	-0.32234188687539	-4.10859423026394	-0.55406856006679
Al	1.03519149130517	0.84948309616653	0.51832104858650
O	-0.55364671628116	0.93005773362666	-0.27947746839242
C	-1.85364521703918	0.94571086585103	0.16921925205669
C	-2.43907765397775	-0.44942407796319	0.35591102302748
C	-2.92589766170384	-1.19735745676040	-0.70599853374847
C	-2.47776575306380	-1.02329823795349	1.62502069720933
C	-3.42546045421507	-2.48240978163414	-0.52740897443287
C	-3.45468266663565	-3.03808134785279	0.74713745866944
C	-2.98179724448705	-2.29571408684793	1.82441274452541
H	-2.09981440994595	-0.46333767953020	2.47432101315131
H	-3.00423375630519	-2.72758918235494	2.81740742752686
H	-3.79303734670893	-3.02269344361629	-1.38997214357048
O	-3.92015883744800	-4.28215412871112	1.02979124733119
H	-2.92374415906107	-0.76992773754481	-1.70212969823950
C	-2.73188950803685	1.75420213013800	-0.77101986438654
H	-1.93808743403041	1.41779945957187	1.16055289030997
C	-4.40980668484030	-5.05651256373429	-0.02567544130535
H	-4.73157802067229	-6.00482037608985	0.40222884908386
H	-3.64688207662320	-5.26246176298285	-0.78539285645072
H	-5.26901729432420	-4.59334243810719	-0.52371113415603
C	-4.07132178507803	1.98917099104592	-0.46122309064134
C	-4.88628250035826	2.72844669855523	-1.29422480750202
C	-4.37432196507808	3.25959939303483	-2.47785714175225
C	-3.04364631022962	3.03628617302990	-2.80005190577144
C	-2.23485090207967	2.29010248834090	-1.94563129574811
H	-4.48520932296913	1.57974815857874	0.45359060017499
H	-5.92321439077495	2.90720318880269	-1.03867074374915
O	-5.24285187806080	3.97434002800906	-3.23937737944284
H	-2.60508146875594	3.43744428837925	-3.70418861121113
H	-1.19416680383025	2.13398643811383	-2.19569683161044
C	-4.75593821086584	4.55655567441237	-4.41374643831439
H	-4.39219661506903	3.81282687979394	-5.13176339443340
H	-3.94646955346689	5.26984602664939	-4.22326018115029
H	-5.58803363352333	5.09320126258098	-4.86741377463739

[(*p*-BrPhO)-**1***-H]$^-$



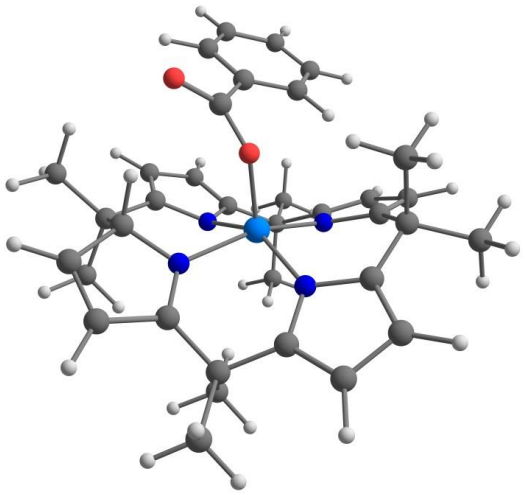
Total correction	0.69736774 E_h
Final entropy term	0.09706548 E_h
Final single point energy	-4433.2581380 E_h
COSMO-RS correction (Gibbs free energy)	-218.4318 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-233.9283 kJ mol^{-1}

xyz -1 1

Br	6.75058632926978	5.65122683561343	14.69479576995522
Al	3.55478979958190	10.48343583192641	10.05192914195296
O	4.86357719806206	9.27545108071783	10.28911187287266
N	3.63772953493993	11.03036137603404	12.05890854524597
N	1.86543585260504	9.60897475757756	10.52926791961452
N	3.08013640664160	10.26541281410244	8.19903018474178
N	4.54231573833630	12.15541742542834	9.76671217320375
C	4.90817914471043	11.31536506624865	12.68189941745816
H	5.61611405768004	10.50248964331178	12.49034140264249
C	4.59448811830355	11.38793744588775	14.13269812395261
H	5.32691737962552	11.54526658067813	14.91001864417804
C	3.27640744166537	11.23514030738462	14.28983431900111
H	2.71713573370959	11.23933530896123	15.21181582322971
C	2.71821452353469	11.03403971963367	12.95790042529443
C	1.26889264011426	10.89567779932335	12.59744853118210
C	1.11643830683230	9.72662136127317	11.66788235276115
C	0.20670447489493	8.69939889535890	11.74767677678614
H	-0.52483226872360	8.53636103266446	12.52408144293770
C	0.39414459210240	7.91520887994313	10.59153500969028
H	-0.16470354436698	7.03242433491364	10.32510109931176
C	1.40526991125144	8.50212347797221	9.86041688183229
C	1.95084592960631	8.01895767156299	8.53444373209317
C	2.43709728935928	9.16636661842143	7.68682204377443
C	2.34905824121126	9.28571454836393	6.31912146744445
H	1.90228636127255	8.58000472065913	5.63641115367060
C	2.94723930011651	10.51653356465966	5.97413217494417
H	3.02793176742412	10.93586157927511	4.98319427700586
C	3.37351010865535	11.08844245912609	7.14889252894741
C	3.88527015339914	12.48319162568083	7.36243861245215
C	4.86515594472587	12.57009376575782	8.49778835917687
C	6.09193849175535	13.18635060342744	8.49786401018958
H	6.60123151550374	13.61146319310786	7.64780856613399
C	6.55095311323410	13.17542848979648	9.83089374877457
H	7.47086302952329	13.61122924195494	10.18904923869210
C	5.58085677395999	12.56060448140864	10.58546037529813
C	5.50799349062997	12.61690610919484	12.09016017338359
C	6.90759276356224	12.78571040215322	12.68415382747506
H	7.56265756352501	11.96363225868565	12.39370850734842
H	6.87644879827416	12.83239099924870	13.77427080295943
H	7.36281006974397	13.71462100060415	12.34325948455639

C	4.64940417462366	13.82923476676990	12.48416939809007
H	5.07401782266701	14.72538592855574	12.03220730212434
H	4.60834850013335	13.97848986164658	13.56599216479569
H	3.62977010697803	13.73568387238583	12.11082932748241
C	0.41475502676343	10.70498664746612	13.84875596293965
H	-0.63419899742872	10.61033764643802	13.57089398442000
H	0.49605476548119	11.56371578227021	14.51767568988925
H	0.69612021328979	9.80691263318557	14.39960004381302
C	0.83335449640305	12.20473766334204	11.90766058181065
H	1.40123670880687	12.39410085119971	10.99743164620169
H	0.96143854134335	13.06704733179853	12.56759224076384
H	-0.21905009044432	12.13306884529757	11.63241594443847
C	3.07381228389555	6.98073668468126	8.73578769830427
H	3.96275291287976	7.42211872017673	9.17234911370605
H	3.36068031551903	6.55859942166973	7.77024228263543
H	2.73826430363450	6.16856382247048	9.38457687700520
C	0.81942541259036	7.29945531502572	7.78682488174233
H	0.47141815441083	6.43252812376342	8.34972480594199
H	1.17243360805945	6.92784857946062	6.82459727146520
H	-0.02754288312715	7.96172561590159	7.61155615864038
C	4.53233827834366	12.99953305697168	6.07795981790976
H	3.81457349439024	12.98912877594128	5.25757064073299
H	5.38527378612928	12.38569001584100	5.78868886452548
H	4.87091798107948	14.02966701273064	6.19996177749720
C	2.68800829024833	13.40283945009542	7.68978001318618
H	3.02112141016408	14.42944182434793	7.86109166857999
H	2.16517473660898	13.06693841840519	8.58542841912771
H	1.96980974501549	13.39685196975531	6.86756378364307
C	5.23808568492078	8.46503651585679	11.24347052937098
C	6.60944734392135	8.24467387842117	11.46154204491832
H	7.31943873828789	8.74865754283186	10.81754853038067
C	7.05850282425347	7.41491683846012	12.47403357614339
H	8.12161145739840	7.27059964263229	12.61653387817902
C	6.14177991097375	6.77921756083956	13.29664043952219
C	4.78220681983974	6.96400105887363	13.09824216522170
H	4.05990050286569	6.46220220425652	13.72867924450902
C	4.33298911615470	7.79218898530422	12.08391623027464
H	3.26735242667292	7.91257382688625	11.93290605790255

[(BzO)-**1***-H]$^-$



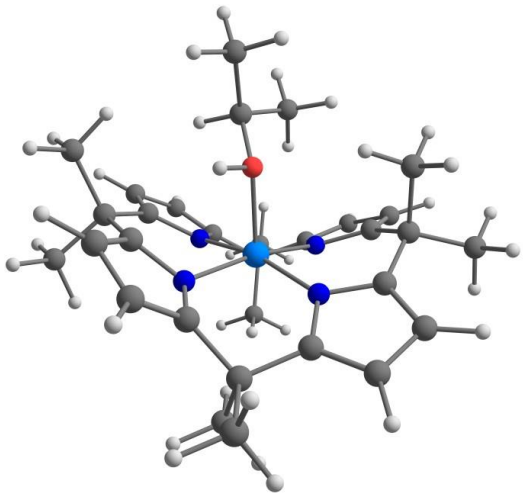
Total correction	0.71913511 E_h
Final entropy term	0.09556558 E_h
Final single point energy	-1972.064719 E_h
COSMO-RS correction (Gibbs free energy)	-216.0284 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-232.7108 kJ mol^{-1}

xyz -1 1

N	1.05970053385755	-1.27294675134670	1.53424110541404
C	2.53184416615173	-1.19611648531581	3.46826982793582
C	2.94468362092916	-2.13738578923228	4.59813580586544
H	3.51096938244612	-2.98921369086997	4.21665394232889

H	2.08125991652748	-2.50974870772308	5.15017975437214
H	3.58980588670698	-1.61388953375316	5.30237490479812
C	3.80744589954675	-0.74298256841216	2.72571632360349
H	4.35283644596918	-1.59391488618300	2.30813904351870
H	4.46217200690899	-0.21948905943454	3.42273731374363
H	3.57963291622104	-0.06021473350787	1.90745794556959
N	1.10128924827692	0.85704642881504	3.20435630371086
C	0.66971397317445	1.88638943601226	4.00110136265407
C	1.78698370380912	-0.00935379506564	4.01229855049502
C	1.06499179484705	1.66041645638630	5.30053270881416
H	0.86861513887836	2.29072285471528	6.15309808109956
C	1.78285781475299	0.44699073022464	5.30851294166864
H	2.24825484848795	-0.01837981783903	6.16368017830188
C	-0.14957014274152	3.04337181198100	3.48523492455516
C	-1.64210033161235	2.65649934209731	3.42092885941167
H	-2.00345860335048	2.39159231976148	4.41736858481150
H	-1.82135335714145	1.80836803382589	2.76715239999873
H	-2.23245806699121	3.49840357155691	3.05166632954377
C	-0.04045762939406	4.20840949902265	4.47652160320260
H	-0.64178784406836	5.05381270080044	4.14085425693738
H	0.99048247001841	4.54281230215909	4.58741230413782
H	-0.42065143862818	3.91976381251254	5.45752033250661
N	0.91548023883111	2.66089241722745	1.21315294901369
C	1.30228349157620	3.41786621514264	0.14617441555557
C	0.36436053610048	3.50700245071640	2.14234560334203
C	0.98747664470368	4.73721000041127	0.37320532163335
H	1.18296742670103	5.57138058925494	-0.28287888193551
C	0.38091052743356	4.79303191471321	1.64817006583019
H	0.02708792969153	5.68113961767560	2.14866339738399
C	2.08118567472145	2.81756010258791	-0.98870054973626
C	2.08203525973059	3.77815555750739	-2.17627159814887
H	2.52401764014467	4.73435132259400	-1.89370026731773
H	1.06892679066276	3.96121687578092	-2.53520836215388
H	2.67394119843417	3.37521778641532	-2.99953327515926
C	3.54309095834582	2.61680798856194	-0.53607580163553
H	4.13922938079810	2.17536866697365	-1.33830938033039
H	3.60335404229959	1.95534760118276	0.32824550493835
H	3.98744659802846	3.57262070090855	-0.25101900290293
N	1.38524611363027	0.44319344525380	-0.53051481226553
C	0.98082691710196	-0.65132520920260	-1.27522128415547
C	1.52357447888607	1.48683038748676	-1.41319089838720
C	0.84203792188363	-0.28170505175175	-2.59237688392125
H	0.54741675817227	-0.91614265880281	-3.41386871137652
C	1.19364369487051	1.07969907904006	-2.68174332375467
H	1.18735505146879	1.68548905496805	-3.57338566947593
C	0.99609806435830	-2.07934582357836	-0.78509336713380
C	0.14055315154062	-2.95873489607212	-1.69903105598377
H	0.53490030186822	-2.96204732383568	-2.71457064913271
H	-0.88836203584201	-2.60078352548112	-1.73050119861600
H	0.13590267436985	-3.99715072992153	-1.36105857682526
C	2.45089698731875	-2.57492238508299	-0.82184177304147
H	2.85060158847160	-2.42750614222958	-1.82493949154564
H	2.53734114776402	-3.63547093806826	-0.57201051201930
H	3.08461352137744	-2.00910119105701	-0.13834014829234
C	1.66756876364124	-1.90827221062703	2.47180493390336
C	0.41892711409369	-2.21718780936570	0.65267985004613
H	-0.65873903247068	-2.01488957975787	0.61175196497162
C	1.44090529088839	-3.34417752447230	2.36914146437928
H	1.81293332995510	-4.09000899363930	3.05361482923763
C	0.68063080763773	-3.53439665589753	1.28524832096797
H	0.31359703442136	-4.47719544755977	0.90799359516611
Al	0.73059334155066	0.74160663222984	1.28810675874638
O	-1.04627798266781	0.48832684216761	1.04936761489804
C	-1.82135873324411	0.24753481516791	0.03719611002665
O	-2.40340892121716	-0.81072900718266	-0.11873245866981
C	-2.00138524648481	1.35240902863598	-0.95924657327166
C	-2.42038814021274	1.02416396425796	-2.24657182105735
C	-2.57412191803328	2.00649638002233	-3.20763802579701
C	-2.32686211688509	3.33591465701351	-2.88727411561759
C	-1.92701245190675	3.67098769348035	-1.60419764546534
C	-1.75947757941005	2.68370984580012	-0.64295779285139
H	-1.44312911719179	2.96915366097253	0.35045529558298
H	-2.60298565279555	-0.01303824616220	-2.49082656059149
H	-2.87942105691823	1.73710897998418	-4.21120081826432
H	-2.44249499419963	4.10665654755265	-3.63987255529280
H	-1.71871576757662	4.69924704687303	-1.34001984249665

[(ⁱPrOH)-**1**]⁻



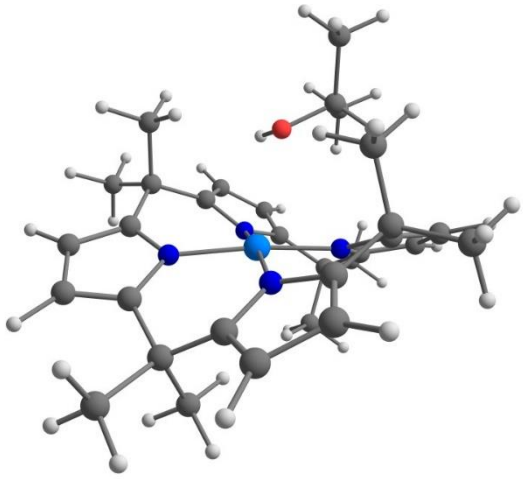
Total correction	0.71017759 E_h
Final entropy term	0.09180514 E_h
Final single point energy	-1745.178815 E_h
COSMO-RS correction (Gibbs free energy)	-203.9993 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-219.0773 kJ mol^{-1}

xyz -1 1

N	1.93879205403122	-1.44831671242939	1.64135904314811
C	3.07555386746541	-1.03412136826257	3.79793479657337
C	3.55060871506090	-1.82820803933087	5.01313525451163
H	4.21499439781318	-2.63721162304306	4.70429124669840
H	2.71150633172072	-2.25918299720443	5.55937291164971
H	4.10700653729525	-1.18930143154398	5.69970281881863
C	4.31681317586315	-0.42300137478630	3.11651276439133
H	5.00452641135641	-1.20470544090918	2.78555887865074
H	4.84095697566963	0.23565012896096	3.81158413307686
H	4.04849907799904	0.16857395060478	2.24099758767937
N	1.25471608874398	0.64460659947367	3.35116351182534
C	0.59484249056286	1.61990451325235	4.06527105231489
C	2.13590417845237	0.05420954280292	4.22392063564359
C	1.05649829546283	1.64171365987186	5.35883260410752
H	0.72095838274715	2.29050047705630	6.15243427944756
C	2.04517168170824	0.64103383730964	5.45991545236691
H	2.61828677410786	0.38619880357840	6.33781132652266
C	-0.54673734078547	2.42814438189571	3.51401673100418
C	-1.85968916591770	1.62943124325413	3.65508294796311
H	-2.06309718393874	1.43689616363771	4.71065712632914
H	-1.80730903717012	0.66756799912388	3.15386773983724
H	-2.69918705589047	2.19181320709830	3.23780690353708
C	-0.71929012948293	3.69472166735130	4.36483656865501
H	-1.56438543357442	4.28629175406079	4.01156981746496
H	0.17358955927692	4.31737776266307	4.33125690702858
H	-0.92594721870732	3.43879797987981	5.40464185129950
N	0.52539684105761	2.15751730795252	1.21731203709701
C	0.60658042004838	2.90470515619357	0.07005915173274
C	-0.28033401941033	2.85122706669604	2.09094349729122
C	-0.16520596075907	4.03310759607292	0.18904703883408
H	-0.28504458000710	4.81321299757156	-0.54658905728551
C	-0.73573896711505	3.99599477426460	1.48010677979142
H	-1.37680509049355	4.74665124670763	1.91532603779825
C	1.51788493204799	2.50720934058951	-1.05240610927887
C	1.29886590502244	3.42100092129412	-2.25523645159952
H	1.51247933643092	4.45811205974426	-1.99335737534612
H	0.27165359878404	3.36573243649737	-2.61674684782645
H	1.96463577196930	3.14225745248862	-3.07329235972889
C	2.98609781261069	2.66276776108398	-0.60668337148543
H	3.66407025964015	2.37686958254971	-1.41378949550084
H	3.22204944068060	2.03727268597546	0.25481362585696
H	3.19073759349762	3.69721801994891	-0.32340419035264
N	1.32249055939793	0.08509183301037	-0.49998773050573
C	1.13352924573622	-1.10159755640921	-1.17070329997759
C	1.25591554169960	1.08208503839538	-1.43502439668580

C	0.91386087116316	-0.84409830584654	-2.50567350718306
H	0.75552970680899	-1.57865221313713	-3.28192403453669
C	0.99939918592003	0.55383313112547	-2.67686733033258
H	0.89617894033006	1.09909867781271	-3.60198666634427
C	1.33669551519212	-2.47857313566859	-0.58937089301512
C	0.22503981682543	-3.42985952097127	-1.05062481249293
H	0.16472020931648	-3.46500599925794	-2.13869748106994
H	-0.75281842831355	-3.12499032301335	-0.67660531299929
H	0.40942561564601	-4.44731157505350	-0.70213154042840
C	2.67716719486608	-3.00854010093876	-1.15760949368144
H	2.66123187783461	-3.01757631193240	-2.24917296242113
H	2.87942000501253	-4.01923689233896	-0.79727237368154
H	3.49675223746670	-2.36508103261033	-0.83863319471597
C	2.38055897132619	-1.94279903251856	2.83335433216014
C	1.47374350445918	-2.51990949075308	0.90935323504113
C	2.15014235766706	-3.29649430184215	2.90377951733567
H	2.39140010433563	-3.95136610565779	3.72643488042562
C	1.55484808903300	-3.66405573962906	1.67652499468686
H	1.30870347227443	-4.66682595287164	1.35875000768006
Al	1.06285687910889	0.30632537297823	1.43100605049710
O	-0.72916733333753	-0.58916868518629	1.42199914187751
C	-1.74812238188476	-0.59796654629913	0.38448393254519
C	-2.84150612003070	-1.55744735060665	0.81839517691081
H	-0.49358499062671	-1.51251780505266	1.62232635117250
C	-2.27475719932390	0.79874120388363	0.14786144606992
H	-1.27970524192046	-0.95359667730933	-0.53699808346466
H	-3.32637658288582	-1.21461377194877	1.73392524677360
H	-2.45717993143591	-2.56608638740320	0.99035702437377
H	-3.59972846164892	-1.62965601711500	0.03847256570900
H	-2.72976681089377	1.22435412660814	1.04056129921739
H	-3.03885171095007	0.74069347834463	-0.62924721185022
H	-1.50478043204283	1.48070287921617	-0.20541267763275

TS-A (coordination of ^{i}PrOH to [**1**]$^{-}$)



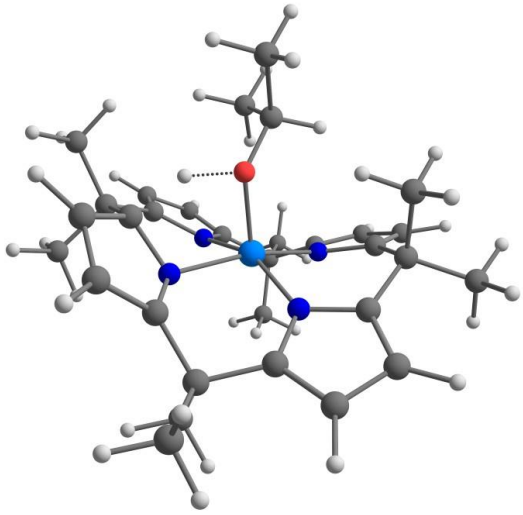
Total correction	0.70930649 E_h
Final entropy term	0.09194390 E_h
Final single point energy	-1745.16337529 E_h
COSMO-RS correction (Gibbs free energy)	-201.5662 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-215.4345 kJ mol^{-1}

xyz -1 1

N	2.40461318958787	-1.70447068366383	2.19527185906825
C	3.87122709764243	-1.06875639740883	4.13464563649157
C	4.50993282083341	-1.77801586054326	5.32788764862479
H	5.28051553971121	-2.47478083603855	4.99633664736734
H	3.76747200954788	-2.33261778366281	5.90115689982560
H	4.99097071348463	-1.05911202766551	5.99197488288907
C	4.99386411932221	-0.31895351610375	3.38213031612713
H	5.75222432502859	-1.01896562747051	3.02575712401574
H	5.46606729314668	0.41878250922926	4.03391764821968
H	4.61346363192841	0.21696772440144	2.51010828575947
N	1.95455680362709	0.50285962402658	3.75309481496843

C	1.31750128448406	1.49942959385189	4.45473717706758
C	2.85862724934227	-0.07329437757971	4.61311261774212
C	1.79378929399575	1.53675642642310	5.74004243613333
H	1.47408753128657	2.20284197946450	6.52596520342997
C	2.78440595483928	0.53342936838182	5.84012338127770
H	3.38262907133491	0.30559423603360	6.70835552873712
C	0.20120006720724	2.30930818150946	3.86266536428581
C	-1.10279914137522	1.49155452437594	3.95155203915174
H	-1.33091010101909	1.27673029196071	4.99751881439065
H	-1.02255176007210	0.53656230952076	3.43645290941369
H	-1.94148716865694	2.04371866783689	3.52074690815504
C	-0.00844284943130	3.57733061287187	4.69529784973800
H	-0.84027079354967	4.16377809579658	4.30295897294720
H	0.88334677449078	4.20288744788412	4.69618264317748
H	-0.25560136531518	3.32495491572179	5.72715684698086
N	1.23279711086663	1.90122118975058	1.57956937631171
C	1.35882794845192	2.58119176384193	0.39771768550319
C	0.53102534195045	2.70703925606380	2.44463801661433
C	0.73279056135164	3.79924278777364	0.49463300165663
H	0.68017146917611	4.56013580732704	-0.26860059444410
C	0.20029211791688	3.87772275071803	1.80241620550967
H	-0.34508170744273	4.70906801679574	2.22110044863179
C	2.17718837821350	2.01998197851932	-0.73195084750550
C	1.98439434618455	2.86626709972204	-1.98756818395941
H	2.30931064684483	3.89241011504344	-1.81171239294245
H	0.93898086583252	2.89052582509814	-2.29710572709804
H	2.57630298905919	2.46892030400752	-2.81332149525603
C	3.67364743830663	2.06242410187010	-0.36329944157984
H	4.28147700903352	1.65881119511513	-1.17565026654159
H	3.89759689198865	1.47557052304271	0.52883676950515
H	3.98779237757331	3.08816206968701	-0.16161952296859
N	1.75462020980875	-0.32540137459622	0.00448692001753
C	1.36670638473873	-1.52838070764142	-0.54580609403529
C	1.75930742790174	0.60253475772172	-0.99910443086782
C	1.10157319388407	-1.33979983466585	-1.88520939424308
H	0.79448240827012	-2.09632498250491	-2.59078937397267
C	1.36606615011105	0.01669876567473	-2.17770305036334
H	1.28730292305325	0.49422003581506	-3.14191504254170
C	1.30291734687489	-2.83553511086025	0.21509216543875
C	-0.12866696443250	-3.18416647158002	0.67962212330903
H	-0.83354655984489	-3.14563944964401	-0.15551844451489
H	-0.48636246470906	-2.51794414908283	1.46161455967825
H	-0.14137410167622	-4.19490825776115	1.09151401354633
C	1.74283251629979	-3.95784284921047	-0.73583846500478
H	1.07239670827972	-4.02539609444307	-1.59335644362668
H	1.71359918934356	-4.92586213680880	-0.23453634898688
H	2.75387362799871	-3.78828604225128	-1.10313106697447
C	3.25612058915179	-2.07604559808738	3.20912849505619
C	2.21539428215448	-2.81666153020830	1.40771923464669
H	-0.62415261626916	-0.62527245371796	0.25421119922892
C	3.57761761314934	-3.40287334853517	3.08279796072812
H	4.23857833188605	-3.96878707554437	3.72022038167038
C	2.90814048695066	-3.87766344019485	1.93392158822547
H	2.93965808283289	-4.88345862731309	1.54550428889311
Al	1.72071488914763	0.07123961972710	1.89427567061360
O	-0.91995039286376	-0.18715924979087	1.06099379919896
C	-1.87082017222523	0.81769682266350	0.71119999023990
H	-1.55693529094197	1.74295790026955	1.20029753164230
C	-3.24157611054679	0.40943484464945	1.23040938874051
C	-1.89399401991923	1.06310698476194	-0.78720462339828
H	-3.21546288254837	0.21266021922915	2.30215399097647
H	-3.59766757227637	-0.49383618328072	0.72968392038319
H	-3.97079273276393	1.20249965999738	1.05418847903710
H	-0.90736206748526	1.34493736158018	-1.15358173720383
H	-2.58530679498122	1.87256592461897	-1.02480965149090
H	-2.22075499508278	0.17328988748452	-1.33337702146862

TS-B (proton transfer from ^{i}PrOH to the ligand framework)



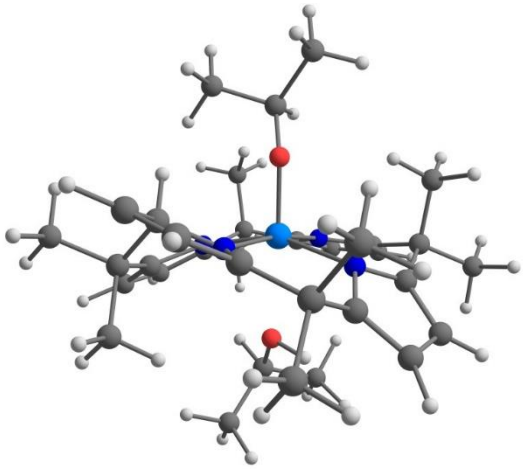
Total correction	0.70271949 E_h
Final entropy term	0.09068877 E_h
Final single point energy	-1745.1580450 E_h
COSMO-RS correction (Gibbs free energy)	-202.2324 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-216.6518 kJ mol^{-1}

xyz -1 1

N	2.06056885354073	-1.55667542964431	2.02801339386417
C	3.45507869316309	-1.28385538981564	3.99433841615613
C	3.88311862248200	-2.09736229961538	5.21402937414184
H	4.34909437168825	-3.03649686814678	4.90822932762658
H	3.03624662755543	-2.32368667132595	5.86196128011753
H	4.61638535959378	-1.54725270354118	5.80350624446589
C	4.71030977630534	-0.96303663188226	3.15927082076610
H	5.20631853431856	-1.87591788131271	2.81936442166135
H	5.41410504433156	-0.38778022720365	3.76231131513790
H	4.46461691023943	-0.37145999995319	2.27824083186470
N	1.91841243276824	0.68610249404392	3.59930326752929
C	1.50889598193283	1.79037171998380	4.30508618101229
C	2.76791626102171	-0.01229309214340	4.41943958968508
C	2.10613685512193	1.79773011530098	5.54457759746409
H	1.96750044860637	2.53056261990628	6.32377025297952
C	2.91268792120874	0.64298229941902	5.61803539626229
H	3.52134858788556	0.33462147315722	6.45426135705649
C	0.41346940130786	2.70845490309516	3.82499274405619
C	-0.94516485278574	2.04788422437333	4.14235287890821
H	-1.08127091934527	1.98039115749757	5.22407143630197
H	-0.99988123727517	1.03515531246322	3.75186492466250
H	-1.76895876363024	2.63083412727067	3.72349624720140
C	0.46440206119139	4.01924541839923	4.61907153443410
H	-0.35108759921749	4.67995974844620	4.32298915353752
H	1.40553351443154	4.54357316027965	4.45822857601549
H	0.34850003525886	3.83097826849521	5.68712683362772
N	1.15886852440393	2.19311002895325	1.45485323338956
C	1.25984346428540	2.86468715344992	0.26574090550457
C	0.56708133172138	3.03932098987749	2.35919452137986
C	0.69224481896957	4.10939646644410	0.39180544131633
H	0.63564164484832	4.87345859625640	-0.36802643176966
C	0.24531253233826	4.21917683815077	1.72822548996659
H	-0.22094977783149	5.08361702137228	2.17506084531087
C	2.09325493203241	2.32080500355607	-0.86272539982184
C	1.89363140781716	3.17535164518428	-2.11250895203056
H	2.17815092994437	4.21027610587354	-1.91881835522256
H	0.85415102913483	3.16232538187070	-2.44118210984305
H	2.51694310581384	2.81255412527614	-2.93097538186209
C	3.58195767056238	2.41101550749317	-0.46409489491483
H	4.21716591378654	2.03495092783729	-1.26937451232463
H	3.79552183598017	1.82228690856869	0.42841686811466
H	3.85942144482916	3.44493920904474	-0.24836477552807
N	1.69267999351978	-0.05171502678565	-0.17120613397532
C	1.40346283137043	-1.25334235944049	-0.77781902792467
C	1.74980797684521	0.88974034922517	-1.16174073626541

C	1.28686955072187	-1.06492731320871	-2.13607618599672
H	1.07067838091060	-1.82376990421680	-2.87385862352635
C	1.51035466822071	0.30526464168573	-2.38392735343105
H	1.49326457217776	0.79731060828985	-3.34382995285086
C	1.32232963048544	-2.59536699697525	-0.08390546061008
C	0.15922352104496	-3.42008521296822	-0.64129980925956
H	0.25588196884982	-3.56072935950765	-1.71760046217222
H	-0.79927667769470	-2.93533904147827	-0.45510054837827
H	0.12890877475060	-4.41439356364605	-0.18953226807215
C	2.63654648688091	-3.35344623399879	-0.35623777037961
H	2.80151881383193	-3.45584894416918	-1.42999341727766
H	2.62227465132306	-4.35166914856295	0.08946736239913
H	3.48476729955586	-2.80779010626368	0.05701596314520
C	2.50640447954294	-2.07586307762549	3.14503629621390
C	1.15179120984307	-2.45758259558278	1.42913496463500
H	0.07797059147058	-1.62368224829116	1.61839444033062
C	1.95071051755664	-3.36605856894943	3.35238030532098
H	2.12452608793215	-4.00709655869034	4.20250838451297
C	1.12584996589263	-3.60434516617935	2.28447926457178
H	0.56314994393117	-4.50892440273674	2.10273457204739
Al	1.40353622295305	0.31566356302113	1.73872500805155
O	-0.31089764931371	-0.43734851838600	1.81514097813597
C	-1.54262741224176	0.06368228054569	1.32754446392159
H	-1.62859269369962	1.10236156902671	1.66437087183007
C	-2.67315543557985	-0.73978034079888	1.95448074649168
C	-1.63691555880295	0.07385566733294	-0.19028803668535
H	-2.61528209209395	-0.71623266136090	3.04328888364462
H	-2.63266923452514	-1.78473013429983	1.63666428081591
H	-3.64377337987373	-0.33913384834966	1.65743122507192
H	-0.85073747175010	0.67604462503408	-0.64299345767496
H	-2.59695224914135	0.50078723883357	-0.48955431994888
H	-1.57098201522990	-0.92938096727851	-0.61221433491272

[((^{*i*}PrO)-**1***-H))-(HO^{*i*}Pr)][−]



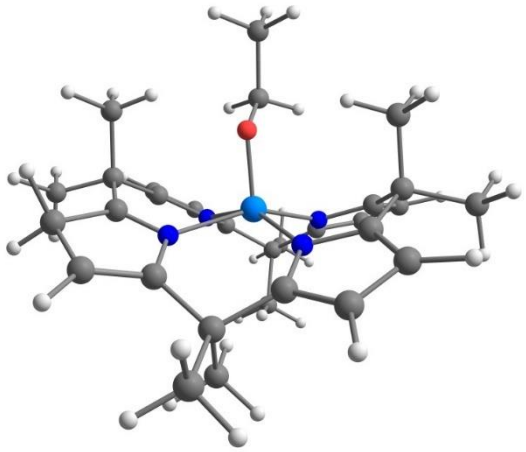
Total correction	0.82925555 E_h
Final entropy term	0.10455905 E_h
Final single point energy	-1939.879559 E_h
COSMO-RS correction (Gibbs free energy)	-199.5404 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-211.3037 kJ mol^{-1}

xyz -1 1

N	1.64064792302641	-1.67379611799296	1.97939563700267
C	2.25731814335927	-1.91343404964795	4.35673649132825
C	1.15250260209118	-2.26286351720958	5.37824371580245
H	0.93605002802762	-3.33396832905581	5.41441091262953
H	0.23402929592573	-1.73162796377005	5.13066686123384
H	1.46829450485348	-1.94606731573239	6.37181143817799
C	3.53965204503867	-2.68352660819731	4.70415906619462
H	3.37799304821336	-3.76303959036408	4.70466818150746
H	3.88623373152113	-2.40926522945230	5.69989012038019
H	4.33591379941562	-2.45739177285786	3.99470877352578
N	1.69707766534951	0.46956135818766	3.75434321785775

C	1.90718198152086	1.67428891038467	4.35617823451612
C	2.49143319633981	-0.43388365229982	4.41406914727064
C	2.86727857631638	1.56494503321835	5.34092514605538
H	3.23767888542812	2.35410312019236	5.97597441477343
C	3.24742804453165	0.20757671206694	5.37625019732380
H	3.93095623616181	-0.24856505475219	6.07742741234652
C	1.07726768100014	2.87085710445884	3.99880939285430
C	-0.40456576463428	2.54718280675109	4.26851000854629
H	-0.55894602578481	2.30303652699835	5.32294048200705
H	-0.73219030476531	1.69721392768152	3.67582652964330
H	-1.02879339080561	3.40657894682430	4.01392251684762
C	1.46253863695054	4.04762435163886	4.89515242811989
H	0.82350705065503	4.90787282875480	4.69344870739749
H	2.49827334331155	4.35203664329760	4.74016945137833
H	1.33404229345857	3.78253802512512	5.94582200635181
N	1.25142237365683	2.33039684072678	1.53399497097108
C	1.40045138962909	3.04682720611232	0.37227927188309
C	1.26606400491356	3.24490404325998	2.55739519566858
C	1.52300062353969	4.38848401532194	0.65920894292883
H	1.65551589914059	5.19274717121539	-0.04686867907505
C	1.43520247947083	4.51507866112923	2.05802796040576
H	1.49747965101114	5.42970741783381	2.62654127271761
C	1.29704791700612	2.45329741364116	-1.00508861359720
C	-0.18906192319721	2.35232923534738	-1.40524514005570
H	-0.65415341008681	3.34049957547055	-1.38571703059808
H	-0.73996850676922	1.71609256256983	-0.72006357944343
H	-0.29002110459580	1.93403195351635	-2.40976136468542
C	1.95492741718762	3.40562283015989	-2.01023136696110
H	1.84426787036963	3.03098550546696	-3.02823019149640
H	3.01704889932210	3.53836193183565	-1.80292390401665
H	1.47622527741829	4.38402406802926	-1.98154543741230
N	1.74240598106312	0.07120952820640	-0.22849023438394
C	2.34735889807293	-1.03166100723973	-0.78369617492924
C	1.93606291292522	1.09633995783378	-1.12218455262945
C	2.94708897791365	-0.70152917272130	-1.97829356795435
H	3.48792706696537	-1.36686336684431	-2.63581108563767
C	2.68374200727693	0.65978634920725	-2.19657988901199
H	2.99181162729778	1.23964223021675	-3.05149473360058
C	2.30465358177431	-2.43794639381320	-0.24128444019231
C	1.86812221171120	-3.39426570939691	-1.36103651924843
H	2.54083378143864	-3.31964932798161	-2.21339449367129
H	0.86553728044347	-3.15190857625763	-1.71686935388239
H	1.87985734555425	-4.43711414708580	-1.03391786172755
C	3.68837990977029	-2.86497756458168	0.26423411021359
H	4.40191482667869	-2.81411705736639	-0.55894805583824
H	3.69406381137135	-3.88802682139040	0.64921496286060
H	4.04673311444730	-2.19587221945253	1.04451498116484
C	1.79518260148079	-2.39605010886952	3.02446222773730
C	1.24965986824340	-2.52256317938956	0.87925802637984
H	0.29500311373108	-2.16471295611816	0.48172716227957
C	1.45349016072916	-3.79719440870716	2.76439347646500
H	1.47663690271866	-4.59417227609008	3.49217095074868
C	1.10669455312199	-3.87557459039027	1.48029548705918
H	0.79459126003588	-4.75785181290166	0.94238782778822
Al	1.28600583593175	0.36698967162644	1.74666095267809
O	-0.43325956831391	-0.10420300840552	1.87441563929703
C	-1.63685320797975	0.24482559720906	1.31012266418367
H	-1.66290080109833	1.31336317893775	1.03337823444559
C	-2.76884455766058	0.02498000600462	2.31571728433064
C	-1.92232249958570	-0.56691163538626	0.04166883707322
H	-2.61675611237661	0.62674806126458	3.21214140459170
H	-2.80720021725930	-1.02379771032098	2.62061681173651
H	-3.74041972430265	0.29151806531368	1.89171381335809
H	-1.10671179292561	-0.46965811817392	-0.67629406609435
H	-2.84414549598274	-0.24240215194586	-0.44829682857661
H	-2.03263737482126	-1.62766355020751	0.28717534208304
O	3.60898881433101	0.47119216704056	1.83839830640286
C	4.52107060395165	1.28080831688313	1.10056201639301
H	3.84692806450281	0.47841281639668	2.77689209931764
C	5.81749701651117	0.51700081764001	0.87323537640779
C	4.75048967485667	2.61662862272613	1.78545833814011
H	4.04219536717609	1.44648524632986	0.13486099472067
H	5.18548676993236	2.48119871166830	2.78069123717632
H	3.82145924315817	3.17486640855344	1.89213526255391
H	5.44390402413311	3.22439345848091	1.20143565884478
H	6.32716329209060	0.30163079772730	1.81693735260923
H	6.50124850112976	1.10131836624069	0.25513785467677
H	5.62367226531286	-0.42366303035407	0.35828436535472

iso-[(EtO)-**1***-H]$^-$



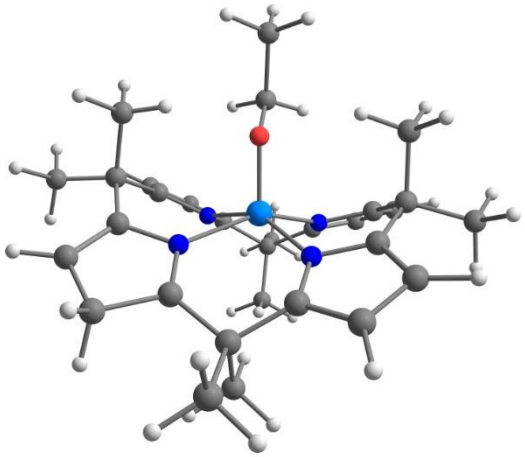
Total correction	0.67904378 E_h
Final entropy term	0.08945330 E_h
Final single point energy	-1705.790843 E_h
COSMO-RS correction (Gibbs free energy)	-222.2584 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-240.4944 kJ mol^{-1}

xyz -1 1

N	2.13613020892744	-1.67699955890317	2.04708922917881
C	3.55188407240640	-1.14620058451289	4.04118673907003
C	4.20054469498707	-1.85201193056251	5.22868944547932
H	4.90984938902996	-2.61041844517812	4.89203652917211
H	3.45557122549604	-2.32870675265716	5.86627110295252
H	4.75458585372405	-1.13592651636997	5.83433185672868
C	4.67155792009688	-0.49980633934566	3.19615773131354
H	5.40112797609950	-1.24554694660357	2.86999771271857
H	5.18292185550967	0.25644381931947	3.79226010330081
H	4.28236326449159	-0.00356091369009	2.30744424634122
N	1.78189934730403	0.59914105537029	3.65221462062281
C	1.21359164708930	1.61938564340432	4.37705398484087
C	2.59561056742049	-0.08885427272157	4.51204846616471
C	1.64508056811797	1.55025573290954	5.68336920435613
H	1.37186698453246	2.21408910625440	6.48801512930149
C	2.53079442668630	0.45882671208557	5.77089571288129
H	3.07286225631085	0.13916641064244	6.64744405577923
C	0.24212083330406	2.63097623502303	3.81136753879210
C	-1.19817297197943	2.08711756955506	3.90737224351792
H	-1.47607568794554	1.95574964700705	4.95627669087575
H	-1.29145461541868	1.12306878485451	3.41829415545040
H	-1.90072894110006	2.78574602098930	3.44693785746776
C	0.28897696829543	3.89800794719365	4.67705357073857
H	-0.42201387481868	4.63730042655831	4.30661636867290
H	1.28210853819749	4.34583200309423	4.67662088954653
H	0.00646172766288	3.67796901560892	5.70731856313727
N	1.20218395458294	2.15663421753482	1.51323141881676
C	1.44704785293597	2.84683190078599	0.36180442187853
C	0.61187253161335	3.01936042110324	2.39792661126837
C	0.99552926010170	4.13953478166147	0.49240700499401
H	1.06175331538677	4.92649788608676	-0.24331653081031
C	0.45785463793305	4.24875794599480	1.79453232396284
H	0.03004955221708	5.13637062559051	2.23452159757867
C	2.26324605266120	2.23790180587181	-0.74460379466582
C	2.16998012472194	3.10813575671365	-1.99640934034474
H	2.52771659515944	4.11684409496382	-1.78681008303048
H	1.14277124899352	3.17889552012733	-2.35448986239715
H	2.78822388407332	2.70207565034225	-2.79867018582561
C	3.74322751154955	2.19839926721567	-0.30820769407138
H	4.36670680412948	1.75885208365885	-1.09066551492121
H	3.87557061111085	1.60506172452500	0.59657299529041
H	4.10369349786615	3.20644792777364	-0.09327476683415
N	1.68374488520667	-0.11156796520901	-0.08774432467687
C	1.36153156258066	-1.28795131194729	-0.71584468284940
C	1.81125103050642	0.83883446233851	-1.06102910049880
C	1.27652796602052	-1.07844538120853	-2.07549652321253
H	1.04514452005165	-1.81098546646924	-2.83423137199435

C	1.56547879849393	0.28271390221748	-2.29597963056428
H	1.59916511342836	0.78469441088925	-3.25004689833605
C	1.15756794613683	-2.62039955648095	-0.03109343514899
C	-0.33236244692585	-2.97364189362252	0.17796727052995
H	-0.85900389141578	-2.86478225919959	-0.77005332295309
H	-0.78584697738203	-2.31434118527751	0.91082624547168
H	-0.44734258423951	-4.00806826957663	0.51481882504091
C	1.76237080172145	-3.72052253802251	-0.92463451165189
H	1.27179599528796	-3.71634747032132	-1.89569829940153
H	1.61257760228896	-4.71550810434912	-0.50052337787954
H	2.82796630191296	-3.56258612290099	-1.09281612617815
C	2.86029209025459	-2.14587896807362	3.17660214689646
C	1.83669263041986	-2.68164705056639	1.30186233746299
C	2.91515584283538	-3.48029722402247	3.18517493086599
H	3.40566435475386	-4.10582418931522	3.91248971984809
C	2.25369451253213	-3.96796315136018	1.95011883038967
H	2.93376958385919	-4.54247909080507	1.31515484782978
Al	1.25311117002172	0.25091201234776	1.79524235268361
O	-0.42775551676285	-0.29203333873440	1.84373454159594
C	-1.36730700960228	0.21913243405201	0.94800600076719
C	-2.76867757058867	-0.26189949798791	1.29745040744376
H	-3.05681543604795	0.05805294597023	2.30012254106574
H	-2.84008284473115	-1.35138287318579	1.26615530657947
H	-3.50049798547795	0.14017804958891	0.59291444198885
H	1.37704754547815	-4.60376032809971	2.11923055053887
H	-1.14403229583660	-0.07777976093128	-0.08969986094390
H	-1.37290736424455	1.31929930098807	0.94273782000009

iso'-[(EtO)-**1***-H]$^-$



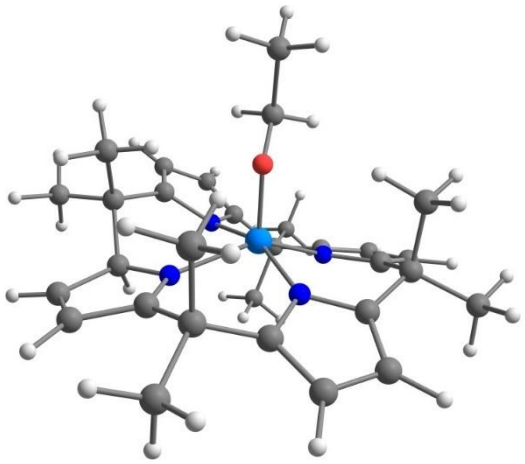
Total correction	0.67913475 E_h
Final entropy term	0.08935310 E_h
Final single point energy	-1705.789258 E_h
COSMO-RS correction (Gibbs free energy)	-222.3674 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-240.7201 kJ mol^{-1}

xyz -1 1

N	2.06609748568074	-1.69003753923991	2.09064296493375
C	3.43836352785042	-1.12767586486144	4.06942374580113
C	3.93096384298045	-1.95291768609035	5.26099323083539
H	4.69352945025423	-2.67623785651776	4.96760751718239
H	3.11173794826006	-2.48458925737233	5.74578967090505
H	4.38534810555805	-1.29672150866799	6.00126629808881
C	4.66030889167824	-0.41632245048829	3.43602696797012
H	5.42022360186269	-1.12564013740354	3.09557998816647
H	5.10929059706121	0.24209249940407	4.17955935529594
H	4.36163342758622	0.19713245502675	2.58696801763944
N	1.67822503557293	0.60777978228463	3.64242099980970
C	1.09630751736252	1.62648836031261	4.35522505191168
C	2.44310286900432	-0.10403685304934	4.52161168109971
C	1.47015019737146	1.53045663286193	5.67861997096353
H	1.16995270037593	2.18405814978427	6.48199742811082
C	2.33553467771645	0.42573541883614	5.78704952036139

H	2.83577872027580	0.08933802088071	6.68215254271817
C	0.17795734794312	2.67185476436792	3.76130527352596
C	-1.28722928994498	2.19603120766519	3.83715948447189
H	-1.58830683347679	2.08482397842417	4.88208531013674
H	-1.41649207476027	1.23491701443349	3.35111848830568
H	-1.94800544060127	2.92454512221410	3.36171469946883
C	0.26804980560582	3.94400152445739	4.61743814294429
H	-0.40229104621618	4.71132726793928	4.22875028681009
H	1.28030537876524	4.34650076265616	4.62993197684812
H	-0.04116246192841	3.74707038193487	5.64475216690325
N	1.17903334291840	2.14307055190369	1.49047538481913
C	1.48092611956292	2.81548677595493	0.34390227340357
C	0.59202768412678	3.03107509562146	2.35203352826672
C	1.06747016573109	4.12334165027255	0.45044694218748
H	1.18040073872166	4.90166166893988	-0.28875800280594
C	0.49565214696415	4.26009171951975	1.73520111936330
H	0.08429573877066	5.16478086507230	2.15583346613427
C	2.31595153266598	2.16844185375215	-0.72458736599696
C	2.30226225605714	3.03161066782898	-1.98473748149239
H	2.68140235713445	4.03046358250536	-1.76549895914944
H	1.29367590383365	3.13100931593380	-2.38621367256070
H	2.94100878882859	2.60194885672916	-2.75799196191909
C	3.77626074041159	2.08313395072359	-0.23124427405164
H	4.41382266374042	1.61811441059049	-0.98707794909625
H	3.85371886249154	1.49006785685088	0.68038100166303
H	4.16180632701723	3.07976394342759	-0.00651809552315
N	1.63122687221621	-0.16529115532626	-0.07944839019627
C	1.31416895327044	-1.33862617286782	-0.72828142567331
C	1.83230678756528	0.78106676679627	-1.04855629752190
C	1.30704297010991	-1.12534344745293	-2.08813944843493
H	1.10628343491190	-1.85472653179302	-2.85752999817788
C	1.63556479843677	0.22946093984377	-2.29279955745714
H	1.72774826468032	0.73030155385220	-3.24356195341928
C	1.07158898656044	-2.66849275441924	-0.04606006230863
C	-0.39457555579659	-2.90948955047089	0.36535267161970
H	-1.04417361061077	-2.75127978776339	-0.49687211135267
H	-0.70495425643838	-2.23626459506443	1.15781209440050
H	-0.52211694061133	-3.93914923473442	0.71014833459354
C	1.44361801356975	-3.79462276093281	-1.01937805632478
H	0.79175514995888	-3.76146139648725	-1.89115541353345
H	1.29990956549106	-4.77414894111384	-0.55901389235240
H	2.47446564229174	-3.71155252152162	-1.36289222311771
C	2.90008341202183	-2.03198291625500	3.00737621992849
C	1.94687686156181	-2.77376733235396	1.16396715405635
C	3.39879167005846	-3.42600022280546	2.80152289743941
H	4.49119116168192	-3.44901698563591	2.73023618281074
C	2.70793733123990	-3.80317771618249	1.54904151088543
H	2.81864083387250	-4.74926882458120	1.04655305025729
Al	1.16331219776397	0.23723275235601	1.78773022515034
O	-0.53699710919493	-0.21730988174455	1.85159596245769
C	-1.44551634126186	0.25490191190995	0.90466945676028
C	-2.85661932730649	-0.21431650643001	1.22818412307935
H	-3.17558925625234	0.14221366262793	2.20913469945820
H	-2.92317720445394	-1.30415619617269	1.23401841173274
H	-3.56662321998200	0.16051057391647	0.48719063456406
H	3.13306464390132	-4.05795698084708	3.65600326031550
H	-1.18939028726242	-0.08316733803951	-0.11196202186045
H	-1.44762379280780	1.35429463427389	0.85684722777071

([(EtO)-**1***-H]⁻)’



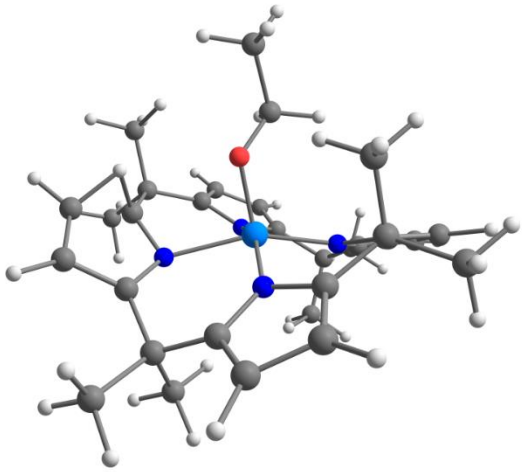
Total correction	0.67959930 E_h
Final entropy term	0.08972258 E_h
Final single point energy	-1705.787333 E_h
COSMO-RS correction (Gibbs free energy)	-213.2083 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-229.0990 kJ mol^{-1}

xyz -1 1

N	2.17906371588659	-1.14135624912097	1.51962875527214
C	2.18508671492837	-1.34180525744693	3.97061750360817
C	0.80242147452898	-1.98384961126455	4.24389417888991
H	0.83094393343640	-3.07131056857971	4.12544340848505
H	0.04517386632854	-1.57919459419882	3.57412830446322
H	0.50744112648558	-1.75556262980733	5.26864285139616
C	3.18620456110099	-1.90210095494116	4.98345430355813
H	3.20795764350642	-2.99263182937693	4.96932085252726
H	2.89177171096808	-1.61004293375520	5.98957716366253
H	4.19587052033375	-1.52905334458834	4.80755940877899
N	1.36375347164633	0.91630213437123	3.22501071622643
C	1.17113834437509	2.12423269379480	3.84146460416935
C	2.07625991732946	0.14604509666966	4.10689291602409
C	1.80896759739233	2.14255070403557	5.06110008551632
H	1.83999319967361	2.96147025537371	5.76180098924274
C	2.38911334916221	0.87137459130801	5.23377244675594
H	2.93908684086809	0.53164528019619	6.09763001539090
C	0.20760198636973	3.14727856398010	3.31314864426383
C	-1.23007526304294	2.61564551147725	3.50587432976630
H	-1.43037290881264	2.44280116625192	4.56646344489147
H	-1.38191142296403	1.67569219086348	2.98041546966745
H	-1.95199858460151	3.34334559813156	3.12805544550207
C	0.32655984028888	4.43428294710659	4.13340125068421
H	-0.40387539909015	5.17138591136552	3.79956195678276
H	1.32002236865488	4.87454933410999	4.04719840847026
H	0.12246765725872	4.23788424823531	5.18692517096014
N	0.86641204268984	2.51305534445701	0.95079484653341
C	0.95381420756461	3.16254265035469	-0.25706355283775
C	0.46054490867783	3.45454509565038	1.86663683326150
C	0.60210938145266	4.48127652164419	-0.11218376427444
H	0.58749621242613	5.23377591777592	-0.88510596463318
C	0.28482442747098	4.66813840081684	1.24811677250622
H	-0.02965418655718	5.58933941499497	1.71290033344172
C	1.50896645690674	2.51525052923792	-1.48855897077646
C	1.13495664969577	3.32995612181616	-2.72581475797704
H	1.52806776989710	4.34435441726685	-2.65477862689248
H	0.05350777803731	3.39189139281774	-2.84848341148208
H	1.55985402507915	2.87970084160386	-3.62431788062960
C	3.05039536402963	2.49158199301770	-1.38831038709338
H	3.48975876050556	2.01606166960289	-2.26900923644938
H	3.37718904578430	1.93845368686721	-0.50814796320036
H	3.44038105525264	3.50820368077051	-1.30497248701135
N	1.24030736425621	0.18764163779560	-0.65247323154707
C	0.96851864618862	-1.04445815852175	-1.20031911258193
C	1.03118108892230	1.10414024243991	-1.64412018359706
C	0.53610274819429	-0.89937202746821	-2.49813420227496
H	0.27594972176988	-1.68815277642896	-3.18807299635965

C	0.57168356118660	0.48230387039604	-2.78247980041766
H	0.33007612238019	0.95075541056431	-3.72360424024679
C	1.38831145261740	-2.31755101419134	-0.51784805127364
C	0.28183278807845	-2.99168433222294	0.30000504380769
H	-0.50811977725439	-3.31672227117360	-0.37920676477957
H	-0.16877046477630	-2.31221438864580	1.01840860633300
H	0.65058853035800	-3.87599835072020	0.82787030483870
C	1.87426204906047	-3.31716897865685	-1.57414263324910
H	1.08101749472480	-3.51764582731902	-2.29289674724181
H	2.14216793927666	-4.27601141472087	-1.12482499061622
H	2.73156813639254	-2.93664675298321	-2.13213713319207
C	2.55491738423934	-1.75873435748775	2.58660808083425
C	2.60085447370422	-1.92491904904598	0.37081798833557
H	3.26562676398912	-1.31223103163774	-0.24961920845338
C	3.30448809495205	-2.97361087649775	2.27464720578003
H	3.74736020293367	-3.64117179400462	2.99598150498810
C	3.34558638467759	-3.06972325198461	0.94604159429804
H	3.83433008760581	-3.83502757476765	0.36248451436791
Al	0.94479413929229	0.59083385185749	1.30293341177252
O	-0.67100074416376	-0.08676355129612	1.48813071762459
C	-1.72054171289533	0.09768209803972	0.59499190770888
C	-2.98651062842902	-0.55702927714017	1.12700153417501
H	-1.49661651194168	-0.32230732749741	-0.39727963136948
H	-1.92382440850686	1.16655110481849	0.42676343904370
H	-2.84245304381178	-1.63109782943264	1.26361439221571
H	-3.82107100400925	-0.41508329012097	0.43634978376506
H	-3.26984336093701	-0.13361909483122	2.09247649287037

TS-C ([1,5]H sigmatropic shift from 2- to 3-position of the dearomatized pyrrole ring, top side)



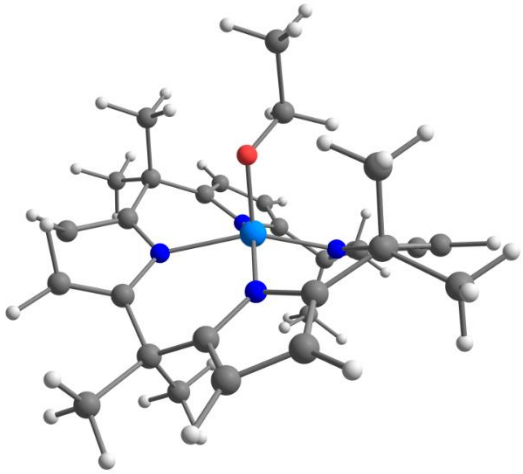
Total correction	0.67504244 E_h
Final entropy term	0.08919158 E_h
Final single point energy	-1705.753477 E_h
COSMO-RS correction (Gibbs free energy)	-219.5222 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-237.5947 kJ mol^{-1}

xyz -1 1

N	2.23214066360445	-1.58221366065805	1.99516322732385
C	3.56351488157775	-1.19612144548211	4.00962401409102
C	4.09267453169519	-1.98418054907666	5.20510387813450
H	4.66101170559376	-2.85662436835175	4.87553559854978
H	3.28451062977462	-2.31813499335348	5.85632261696647
H	4.76226514023413	-1.36410974474096	5.80029434347266
C	4.76471576678167	-0.71140450370668	3.17445270742051
H	5.36848821585961	-1.54993758773800	2.81718582057749
H	5.39325779572706	-0.06631683374566	3.78891478444899
H	4.44677000284978	-0.13483233967854	2.30703689783418
N	1.88710699444048	0.64954932700487	3.63271138931553
C	1.38306021192422	1.70283082098002	4.35610199896094
C	2.73630078735711	-0.02642906330440	4.46712454551829
C	1.90824965372922	1.68413070724292	5.62934421739538
H	1.69691181619829	2.38161667806402	6.42419877664058
C	2.77490379212673	0.57571316791437	5.70195283776428

H	3.36150400196906	0.27012839508209	6.55486739798003
C	0.34084114247133	2.66007705017229	3.82855368464479
C	-1.06036878201210	2.03057201688770	3.97497604615861
H	-1.29202313223267	1.88137186388956	5.03265512462340
H	-1.11652584872030	1.06219458091753	3.48712451627176
H	-1.81933481815772	2.68647951214527	3.54209676120051
C	0.34399387893324	3.92912549554593	4.68930471158017
H	-0.42268566912832	4.62403567301688	4.34486152345539
H	1.30806270392352	4.43542582411656	4.65225413937783
H	0.11387600437766	3.69365419884943	5.72923557989477
N	1.20095989323713	2.19843639343699	1.49276345062501
C	1.39350369201253	2.89751520047889	0.33398607304194
C	0.63727768614470	3.05496150558339	2.40197014582468
C	0.93118167926805	4.18307088269273	0.48708284666374
H	0.96000253179463	4.97283843966383	-0.24790941254771
C	0.44386226816011	4.28275623501530	1.80964584355906
H	0.02453568342791	5.16387198883871	2.27014965963343
C	2.18199776886325	2.31404882391324	-0.80568940978400
C	2.03161412476093	3.19281725883005	-2.04567920082742
H	2.38341216269825	4.20493368412256	-1.84248572122868
H	0.99126714325151	3.25158282494874	-2.36615474626538
H	2.62555367483864	2.80003978885287	-2.87252621432422
C	3.67637482802451	2.29690517048197	-0.41818999345635
H	4.28088999233868	1.88093779946392	-1.22788608455102
H	3.85049425133922	1.69146561890048	0.47169695642772
H	4.02520024984139	3.30835277148422	-0.19984322156756
N	1.67116967135479	-0.04104728337841	-0.14250125437405
C	1.34524914053315	-1.21882053551030	-0.76042250029215
C	1.74546791506121	0.91082048502006	-1.11792423983027
C	1.20683888566240	-1.01242168041477	-2.11600360475580
H	0.96083434681002	-1.75604459369477	-2.86116928921651
C	1.46624850026443	0.35325383787471	-2.34589264169306
H	1.45197833063494	0.85934470170148	-3.29831918938870
C	1.23606408170288	-2.57541908037217	-0.10605600052043
C	-0.14564825108016	-3.19201844540329	-0.35670018158167
H	-0.33882893994647	-3.25380913808897	-1.42646938753524
H	-0.92777892108810	-2.58053011792096	0.08956056354128
H	-0.22242798741732	-4.20680521970487	0.04660072618662
C	2.31269073226752	-3.49295501253361	-0.72915949786675
H	2.18140650303323	-3.54423462121670	-1.80894854696898
H	2.26063609746442	-4.50967308499116	-0.33029707441114
H	3.30959990046054	-3.09660081083158	-0.53677918049610
C	2.71342549628935	-2.07502737504261	3.14921535158778
C	1.53925508062974	-2.56287406841549	1.36995719052717
C	2.29657061024455	-3.37914280874447	3.35681964953271
H	2.46753260009776	-3.99308544656267	4.22452598223899
C	1.52440093816274	-3.71521785180547	2.23204082813275
H	1.10556295809474	-4.67496510255129	1.96829159450009
Al	1.33423417211243	0.29670809614272	1.76901477922977
O	-0.30182674718017	-0.38957671298158	1.87931203767691
C	-1.34333152400327	0.05068070440329	1.06808067037837
C	-2.65529926911503	-0.59839487607080	1.48408389855540
H	-2.90908069083657	-0.34316828663329	2.51446297550087
H	-2.59770651337693	-1.68805888720896	1.42101540434209
H	-3.47552298599817	-0.26943123575759	0.84205051874859
H	0.50897351142291	-2.83327799622740	2.10649045084828
H	-1.15706373747882	-0.17640258309512	0.00577813363566
H	-1.46940360568233	1.14305042131495	1.11461372294208

TS-D ([1,5]H sigmatropic shift from 3- to 4-position of the dearomatized pyrrole ring, top side)



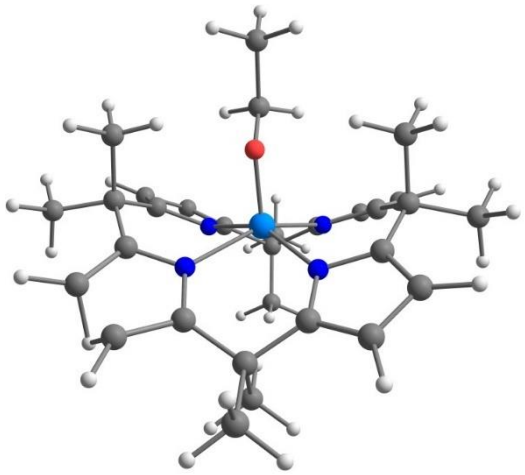
Total correction	0.67527549 E_h
Final entropy term	0.08905227 E_h
Final single point energy	-1705.743666 E_h
COSMO-RS correction (Gibbs free energy)	-228.1999 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-247.8355 kJ mol^{-1}

xyz -1 1

N	2.18614575752033	-1.65717331318152	2.03785101170519
C	3.56543240118840	-1.10678567917740	4.03509183092814
C	4.16371755272359	-1.86378044595521	5.21912508747537
H	4.90063905133625	-2.59919472655660	4.88869530983361
H	3.39526172799061	-2.37242022179473	5.80221196327744
H	4.68178395769844	-1.17130491381070	5.88083146565072
C	4.72124769249131	-0.43289915369330	3.26346878758473
H	5.45029979181263	-1.16803686395956	2.91185980228646
H	5.22656390181424	0.27890968641582	3.91688879363253
H	4.35785173940591	0.11820173529088	2.39681175153140
N	1.78380567338306	0.61579891557988	3.65111829680430
C	1.21006684641477	1.63506276091924	4.37199749166896
C	2.60023257944670	-0.06270989601550	4.51201796411610
C	1.64309588004319	1.57445337859090	5.67853165331003
H	1.36404358411852	2.23815223226107	6.48130843871032
C	2.53563142080669	0.48886910028041	5.76998434884304
H	3.07984295884099	0.17606999097018	6.64792532518812
C	0.23276462395019	2.63774253797656	3.80191745527598
C	-1.20482646670572	2.08932814570025	3.91053400682644
H	-1.47846920018014	1.97050192356869	4.96213307796512
H	-1.29426894531379	1.11872873504757	3.43407751203762
H	-1.91224309241111	2.77862663058356	3.44357037212110
C	0.27953257248955	3.91256270445811	4.65662005354094
H	-0.43631010471271	4.64607980977511	4.28411296727695
H	1.27091377307617	4.36410268847649	4.64661919918218
H	0.00368159033726	3.70033782861385	5.69040174371747
N	1.20159547322890	2.15527054306657	1.50665378816314
C	1.44111017170315	2.84179881442867	0.35227307119025
C	0.59588255109623	3.01557087760889	2.38368004665717
C	0.96999917761830	4.12858301681119	0.47191070672278
H	1.02775035250037	4.91153553925880	-0.26876676425966
C	0.42574032947482	4.23843605647535	1.77111339525952
H	-0.01586954317149	5.12293846618725	2.20378104783288
C	2.27166897040687	2.23702958131175	-0.74495184901963
C	2.19075206138404	3.10958650616579	-1.99602777306531
H	2.54064173585634	4.11965530217856	-1.77942282806428
H	1.16810646245695	3.17561068485542	-2.36783534466697
H	2.82151098108894	2.70846432163436	-2.79089909734073
C	3.74675676381181	2.20242903326823	-0.29162035972762
H	4.38040280979951	1.76842658368087	-1.06890767936123
H	3.87159438299481	1.60504225011385	0.61166446217768
H	4.10091660786110	3.21093726396461	-0.06803355557318
N	1.67598927266626	-0.11385698983468	-0.09894545287598
C	1.37934344711995	-1.29392287406603	-0.73668211796578
C	1.82896718892283	0.83664645062687	-1.06915187640516

C	1.33519097629004	-1.08283183029036	-2.09808298818424
H	1.13022750545475	-1.81543122827541	-2.86390785998358
C	1.62328119739774	0.27951684209101	-2.31033796952136
H	1.68291730265718	0.78165151394266	-3.26308948861823
C	1.14970581085739	-2.62709915944110	-0.05858817952382
C	-0.34244130852212	-2.94595992916883	0.16398692245140
H	-0.88898940964589	-2.81616584612283	-0.77074495824855
H	-0.76896215715489	-2.29078980225497	0.91593851640657
H	-0.46769895795946	-3.98137472166895	0.49463106545426
C	1.71367256731436	-3.73052385303645	-0.97260356889463
H	1.19879635491222	-3.72131758786265	-1.93162617660949
H	1.55563684324591	-4.72470893398824	-0.54868508643354
H	2.77797951827459	-3.59153331557563	-1.16052366120846
C	2.90345897228241	-2.06599702912178	3.09774712023531
C	1.87051171373351	-2.70821771317335	1.25746791921217
C	3.01913375129986	-3.45389816895983	3.08756456797274
H	3.61219989134965	-4.09079847419700	3.72217200157023
C	2.32771125138442	-3.88346487013247	1.85373216664798
H	2.33278226677178	-4.88727073823055	1.46438804098962
Al	1.26121805455795	0.24706218539659	1.78846533275213
O	-0.41882259087731	-0.29380344038533	1.86644585354527
C	-1.36862946913127	0.20643768537368	0.97530297510433
C	-2.76428337654033	-0.28223367438366	1.33723540559130
H	-3.04767000983354	0.04003073365233	2.34058066029885
H	-2.82825374736489	-1.37220064312340	1.31038574159622
H	-3.50367254876375	0.11238815236770	0.63633967727032
H	1.81647331721138	-3.89841044882643	3.04618013473407
H	-1.15179573755159	-0.09354818077104	-0.06261232390540
H	-1.38133444603555	1.30658745806587	0.96519062912979

<u>TS-E ([1,5]H sigmatropic shift from 4- to 3-position of the dearomatized pyrrole ring, bottom side)</u>



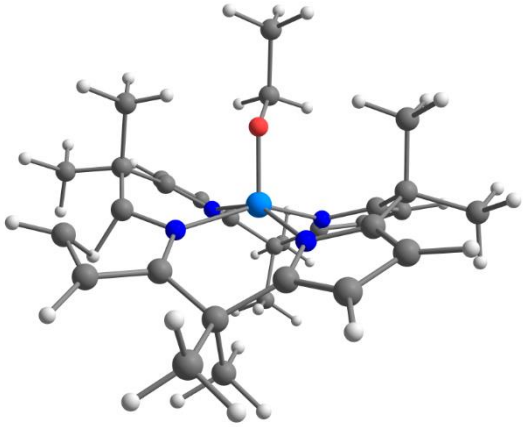
Total correction	0.67583717 E_h
Final entropy term	0.08741234 E_h
Final single point energy	-1705.743259 E_h
COSMO-RS correction (Gibbs free energy)	-228.8232 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-248.4162 kJ mol^{-1}

xyz -1 1

N	2.13014381652094	-1.69286064980186	2.07509153596785
C	3.55279033076982	-1.10292679952901	4.04187890575874
C	4.15314010517141	-1.86325669015860	5.22386627606196
H	4.92727858479240	-2.56065474382574	4.89691684457418
H	3.39105947219546	-2.41599839756004	5.77408772622900
H	4.62760976824579	-1.16680625458940	5.91355479090022
C	4.70156596240984	-0.37127106403092	3.31150276028023
H	5.46688867598127	-1.07212126703399	2.96573868997941
H	5.16500231217979	0.34631457540821	3.98920376623767
H	4.33757908848401	0.18361907854808	2.44729842229620
N	1.75707118343621	0.60135333604168	3.65410347621575
C	1.16648950512051	1.60753347284406	4.37831168242311
C	2.54972910484989	-0.09745652394905	4.52111287219068
C	1.56014762775644	1.51515398349321	5.69590732559865

H	1.26037390852432	2.16221299661359	6.50483428816150
C	2.44833238763055	0.42629212590088	5.78865207019206
H	2.96858359561409	0.09603513430532	6.67463435775477
C	0.22149389897315	2.63726939979014	3.79994418056716
C	-1.23250693058904	2.13119501965030	3.89334612463877
H	-1.51811426398074	2.01290522787325	4.94178919155940
H	-1.34662629443905	1.16739157821188	3.40859038339878
H	-1.91495522563415	2.84507077489364	3.42619435520173
C	0.29783331593536	3.90823765577256	4.65922065544011
H	-0.39351123861939	4.66338524738328	4.28358783062041
H	1.30193531083019	4.33080909474824	4.65845975208853
H	0.00804619534127	3.70138500658934	5.69021510163287
N	1.20317736801773	2.14138794416476	1.51144511609450
C	1.46172824611710	2.82402363227992	0.35967583323967
C	0.60683921748507	3.01057427261958	2.38578262759611
C	1.01363153639455	4.11941895103376	0.47777853965709
H	1.08938186619119	4.90188780766086	-0.26183620536016
C	0.46315829343892	4.23740197313685	1.77356362668795
H	0.03364872718730	5.12896347611734	2.20397668419284
C	2.28531575365559	2.20272745530464	-0.73362287568031
C	2.21938389799418	3.07175890491792	-1.98808278236658
H	2.58304105201106	4.07744700193397	-1.77388569109297
H	1.19848502768922	3.15137202279688	-2.36192050452646
H	2.84594919573034	2.65919493707297	-2.78046912124010
C	3.75907386846949	2.14829888217550	-0.27822406339778
H	4.38775944075362	1.70194117970814	-1.05266465070132
H	3.87329703156152	1.55329697077138	0.62795639112332
H	4.12748111710915	3.15245087795148	-0.05826915737507
N	1.66421861410473	-0.14286542987344	-0.08240704508143
C	1.34705933084661	-1.31794520624695	-0.72062923370535
C	1.82287722739271	0.80734071294711	-1.05348263083138
C	1.29708060419990	-1.10534456654814	-2.08088007008489
H	1.08042041257486	-1.83551037375697	-2.84568085225469
C	1.60160571910759	0.25390171949431	-2.29357823072470
H	1.66254549901215	0.75598708084518	-3.24627700739605
C	1.11843820144367	-2.64733631805272	-0.03282395267935
C	-0.36320015028698	-2.93193718408159	0.28629988587677
H	-0.96278910152820	-2.79864525266803	-0.61518738094537
H	-0.73140538670808	-2.26149727322608	1.05565631087606
H	-0.48641266161990	-3.96193731944219	0.63347734307888
C	1.59083954923678	-3.76566802682378	-0.97521101264676
H	1.00820326154648	-3.74636781278171	-1.89445308692658
H	1.43633518714336	-4.75320216905408	-0.53459621342906
H	2.64196660015697	-3.65640490926334	-1.24214588306037
C	2.94830017257293	-2.06972375522046	3.07105439368426
C	1.91588155045721	-2.72632550424429	1.23715878108915
C	3.28434460492108	-3.41710341926255	2.92960069773775
H	3.80546949568739	-4.06028194868475	3.61876271734883
C	2.58968127462359	-3.85575365501118	1.70442070921192
H	2.52993314454066	-4.87087897115278	1.34939787819083
Al	1.22966266391242	0.23295156898036	1.80039940159958
O	-0.46355512635327	-0.25743518837469	1.86565074452850
C	-1.38772807868134	0.23885440581064	0.94604331197042
C	-2.79528165391915	-0.23224244858121	1.28361488134442
H	-3.09700191860673	0.10483893887451	2.27671305673327
H	-2.86750388466587	-1.32175193988485	1.26829179058526
H	-3.51572104617664	0.16057646391191	0.56221755434704
H	3.83530473223656	-3.51641269714938	1.77022666932328
H	-1.15121677254375	-0.07829580377083	-0.08232822744897
H	-1.38809390193420	1.33884867505699	0.92090756686822

TS-F ([1,5]H sigmatropic shift from 3- to 2-position of the dearomatized pyrrole ring, bottom side)



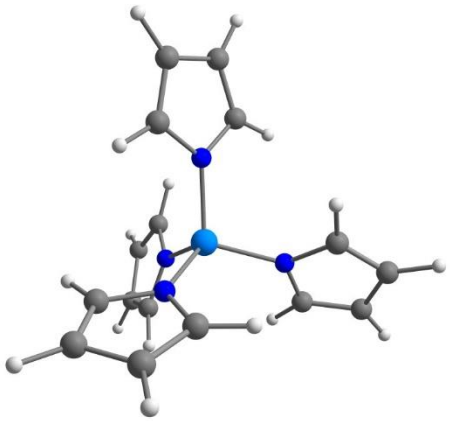
Total correction	0.66835617 E_h
Final entropy term	0.07769826 E_h
Final single point energy	-1705.752109 E_h
COSMO-RS correction (Gibbs free energy)	-224.9765 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-243.8171 kJ mol^{-1}

xyz -1 1

N	1.65358579352905	-1.48390367120637	1.67025928020529
C	2.84429720839396	-1.03328387195454	3.80253524454641
C	3.27072797882073	-1.84616916345708	5.02445705428579
H	4.06207507420443	-2.55580574072555	4.77725441630317
H	2.43150550565351	-2.39428872745772	5.45294415667294
H	3.66935676467020	-1.18433092352728	5.79167134950971
C	4.09551717839824	-0.32542691514804	3.23384045718176
H	4.86754920204739	-1.04435500114351	2.94566475297351
H	4.50557533811774	0.34518480624705	3.98943796115270
H	3.84927712801727	0.27817065342742	2.36055537479492
N	1.16397975015076	0.75474152404804	3.26315612369482
C	0.53943717228999	1.76663330455398	3.94855000106868
C	1.82719322452718	-0.00125789985395	4.19061398437612
C	0.78181733207088	1.62524472147594	5.29787010503199
H	0.42166814097192	2.26412434171598	6.08854036266431
C	1.60816939334102	0.49639502023473	5.45419522897543
H	2.01285702367440	0.12267615131166	6.38207865020784
C	-0.30029653410550	2.84712466345611	3.30541189428462
C	-1.78034864591598	2.41360178144517	3.27506705421372
H	-2.15518662974016	2.29894232630036	4.29538579314415
H	-1.90016876510849	1.46090387102554	2.77017283642806
H	-2.38743099283406	3.16439312253504	2.76394647779776
C	-0.22989804230251	4.10628258207078	4.18301768801817
H	-0.85188457679920	4.89847215252271	3.76491170100262
H	0.79080096660406	4.47794987551017	4.26543825406462
H	-0.60856257513644	3.90569251438558	5.18589323611732
N	0.82266533555624	2.32526497434007	1.08438939681198
C	1.17329849998056	3.00681564584701	-0.04459641801640
C	0.20833670872474	3.21224451299309	1.92918156109036
C	0.77207836395651	4.31811032930584	0.06013545647089
H	0.91997852808469	5.10149267444560	-0.66742431443995
C	0.15142892931870	4.44837208581207	1.32195581905026
H	-0.27010372746627	5.35243118032717	1.73353498014920
C	2.01600197948704	2.36085700471352	-1.10794255271156
C	2.05334958313939	3.24755159346356	-2.35084479265009
H	2.46087350121740	4.22932325729975	-2.10693273170240
H	1.05593438485449	3.38759859710640	-2.76793900112179
H	2.69115458659361	2.80999779606021	-3.12065375866558
C	3.46223325791267	2.22056736431996	-0.58717093192825
H	4.10237200926177	1.75488698455835	-1.34069070324812
H	3.50464326327421	1.60523617758478	0.31196012885174
H	3.87153957322656	3.20033365578811	-0.33256019967155
N	1.27933110003996	0.04264434067977	-0.51579920778484
C	0.94086086572487	-1.11116261531380	-1.17903838140103
C	1.49721186266316	0.99625063854843	-1.46825679991488
C	0.92917304108100	-0.88180256729551	-2.53758507123141
H	0.71218127232107	-1.59659950460649	-3.31705981427934

C	1.28497742328156	0.46934459565485	-2.72272528329060
H	1.38724623599780	0.98247894996103	-3.66592256654179
C	0.71925462260849	-2.44081422641683	-0.49712527604616
C	-0.74129432437436	-2.74157221778196	-0.11477472502513
H	-1.37127070936246	-2.64446413774899	-0.99980044927831
H	-1.09990825284368	-2.05150528628746	0.64256447829237
H	-0.83465625044124	-3.76367211732819	0.26337805520747
C	1.17109157129830	-3.55955465736594	-1.44716241105108
H	0.56227007621029	-3.53831495475047	-2.34872221087789
H	1.03339061176609	-4.54828749915679	-1.00414351019163
H	2.21213857486596	-3.44650723028199	-1.75580733857681
C	2.34438543988300	-1.94974850546855	2.72709569941444
C	1.55564838045421	-2.48732153964852	0.75624151446512
H	2.75012992311560	-2.82122612969159	0.40733106230774
C	2.69600479174438	-3.28209370215960	2.56060946630611
H	3.29484107509576	-3.88860077392417	3.21740115088066
C	2.20893711162625	-3.65527187214821	1.30609118704135
H	2.22205965884956	-4.62661717653547	0.83749040992537
Al	0.77731757239220	0.41482252375166	1.36913568076005
O	-0.93059747875509	-0.02945277550941	1.32413618656235
C	-1.78810579110251	0.46916492764099	0.34458200833837
C	-3.21881521996397	0.01369241358351	0.59540524435356
H	-1.49123820305587	0.14346623630470	-0.66518910740941
H	-1.77464541155486	1.56909158527837	0.31354850944826
H	-3.29944993837177	-1.07529535115963	0.58035880006866
H	-3.88928858280176	0.40919402736665	-0.17128790557624
H	-3.57864923905484	0.35796927005190	1.56646922811929

[Al(pyrrolato)$_4$]$^-$



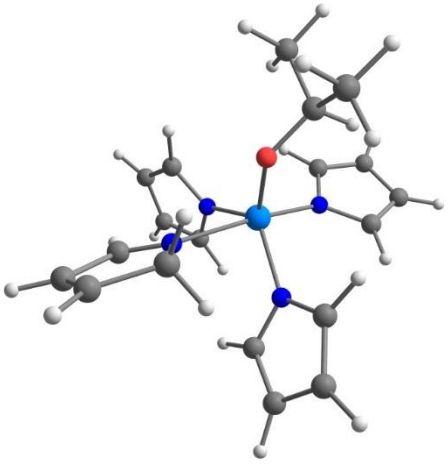
Total correction	0.31739921 E_h
Final entropy term	0.06634157 E_h
Final single point energy	-1082.707964 E_h
COSMO-RS correction (Gibbs free energy)	-188.5814 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-204.4565 kJ mol^{-1}

xyz -1 1

Al	-1.33224466407753	0.84174815051162	-0.03022587446241
N	0.03247845664727	-0.05997682999850	-0.87976998958928
N	-1.99979917026661	-0.59546487438964	1.12613923501251
N	-2.83452460564934	1.23093231874035	-1.01692586812740
N	-0.86033601314796	2.22634845150022	1.08073232665115
C	-3.73718583453873	0.32180456097723	-1.51382771762033
C	-4.75201440680994	0.98210002721833	-2.15237911181761
C	-4.46751811806224	2.36682050193547	-2.04850385201313
C	-3.29393887353974	2.47915433140073	-1.35329569851359
H	-3.58474881273287	-0.74101387780401	-1.39544262549067
H	-5.59792746027641	0.52793870333872	-2.64333218128401
H	-5.05579844034028	3.18141112946674	-2.43922191806810
H	-2.74864355298595	3.36499291292218	-1.06602277722964
C	-0.15238220629122	-0.77059618520142	-2.03950992301044
C	0.84761300304271	-1.69734190261114	-2.17728306561583
H	-0.98055415278198	-0.55160055733068	-2.69662119664173
C	1.69288005359894	-1.55865311990433	-1.04812762364962
H	0.97312304163530	-2.38055291726935	-3.00191770959099

C	1.16406052247356	-0.55417588972028	-0.27963570798426
H	2.59303119091725	-2.11420852677516	-0.83807806141575
H	1.52088963128978	-0.15309722798350	0.65716520160388
C	0.39641947618192	2.58948144864351	1.49116862163786
C	0.30549244071793	3.50511450365767	2.50461931312906
C	-1.07514930798805	3.72246898319064	2.73749773159808
H	1.27548019998268	2.18698855907820	1.01208665640488
H	1.13154503233823	3.97741310039028	3.01147091809125
C	-1.75494894638631	2.92876182224714	1.85265961320881
H	-1.51420435290553	4.39729273840634	3.45486366522231
H	-2.81924233463964	2.84510253061241	1.68681214684080
C	-1.59826236491649	-1.82100497131531	1.14735672065213
C	-3.24390946494556	-1.80002795745421	2.66003851539952
C	-3.08205074100111	-0.44959364588010	2.07364871137782
H	-3.98141396437290	-0.09791449249483	1.55558678990559
H	-2.82582633617720	0.31629534691294	2.81446013661843
H	-2.18461404247999	-3.66829452345131	2.28419444837614
H	-3.97382952699003	-2.04878205513682	3.41525962539242
H	-0.78672511123810	-2.16040052763721	0.51274949298034
C	-2.34460024328382	-2.61930003879293	2.09394103202180

[Al(*i*PrO)(2*H*-pyrrole)(pyrrolato)$_3$]$^-$



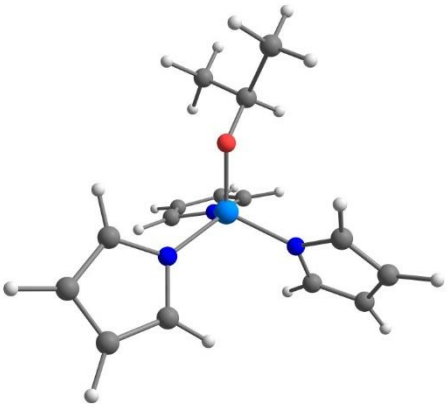
Total correction	0.43602076 E_h
Final entropy term	0.07785621 E_h
Final single point energy	-1277.384344 E_h
COSMO-RS correction (Gibbs free energy)	-203.7190 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-220.2146 kJ mol^{-1}

xyz -1 1

Al	-2.33380797277054	0.40919620589848	-0.00857630508448
N	-1.07534189801080	-0.74456867889504	-0.87955976476872
N	-1.84350948793238	-0.85123749896637	1.77777177929741
N	-2.58019016509518	1.56422244806719	-1.54705285538993
N	-1.78326162323731	1.79273296394388	1.21527428646443
C	-2.70021989994844	1.11248879953294	-2.82722320493802
C	-3.16248487267815	2.11676629610386	-3.64781701123198
C	-3.33587976522154	3.25391567232419	-2.82350406450829
C	-2.96915531859309	2.86980482752699	-1.55280705443803
H	-2.42772476213684	0.09895619234689	-3.08128837740363
H	-3.33756618684869	2.04532050123695	-4.71110218518088
H	-3.67000935438735	4.23611030730672	-3.12395491211579
H	-2.94047732952130	3.45911168716640	-0.64934712541610
C	-1.27784141193332	-2.05715846553861	-1.17724811460204
C	-0.11261660773007	-2.61764013054454	-1.65487570856122
H	-2.24276275935980	-2.51449168200267	-1.01641827259147
C	0.85687704339706	-1.58687959164709	-1.64919195316728
H	0.02011375363710	-3.63797049817309	-1.98181804489594
C	0.22078380207970	-0.45993452953484	-1.17515503483060
H	1.88471739248331	-1.65370155578182	-1.97196135599347
H	0.60797541474530	0.54090360671001	-1.05369208223829
C	-0.56240297773428	1.95787413869108	1.78868986711839
C	-0.64824682729317	2.82907450097131	2.85245343778655

C	-2.00559729227831	3.21932303807260	2.93676523557737
H	0.30177028649963	1.42934623463410	1.41342556931853
H	0.16639140308464	3.15446327530393	3.48145050920841
C	-2.66066243620068	2.56128099268417	1.91708770220483
H	-2.44630034199007	3.90714325937986	3.64254850762314
H	-3.70732978602752	2.58759291107503	1.65187514919138
C	-0.92751936553365	-1.72513288118603	1.96623050094035
C	-0.89898407151089	-2.21513807957109	3.33830433698808
C	-1.87411123505417	-1.56955256339992	3.99154803939856
C	-2.52872787994548	-0.64763327382958	3.02860252258735
H	-3.59668951236753	-0.83608553079847	2.88622413843384
H	-2.44018824796110	0.40461278803060	3.32760954566164
H	-0.21124461424728	-2.95122392783604	3.72652147553730
H	-2.14728921696413	-1.67040030952948	5.03160834897168
H	-0.26949232237623	-2.03836758092716	1.16438040356831
O	-3.95564792005880	-0.20085492422014	0.26029169654764
C	-5.12601655998367	0.05169421311059	-0.44626630095392
C	-5.45055960311526	-1.11614986317385	-1.37357654141614
H	-5.03591463673667	0.94917669618031	-1.07577165899363
C	-6.26771873853040	0.29374128474761	0.53828986239557
H	-4.64665823582223	-1.25862488110388	-2.09684044708933
H	-6.37254680562749	-0.93887638838424	-1.93252617453966
H	-5.56806062184672	-2.04242610417368	-0.80484504377942
H	-7.20514091330258	0.50827967108426	0.01989544571079
H	-6.04200146070664	1.14240154583970	1.18666313176101
H	-6.42477805730644	-0.58198511875213	1.17365810183567

[Al(ⁱPrO)(pyrrolato)$_3$]$^-$



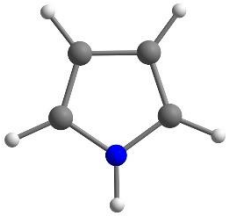
Total correction	0.34515505 E_h
Final entropy term	0.06889804 E_h
Final single point energy	-1066.862885 E_h
COSMO-RS correction (Gibbs free energy)	-191.9732 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-207.6408 kJ mol^{-1}

xyz -1 1

Al	-2.32787089376532	0.82705298236956	-0.03176798616917
N	-0.72027642196658	-0.13098925109499	-0.05198552017321
N	-2.69484432964207	1.40530583823144	-1.78493792384843
N	-2.14455272357570	2.39653377244750	0.98088437084716
C	-3.63563406779807	2.32677802891561	-2.14669524078630
C	-3.80485210954831	2.31212938684528	-3.51012704153960
C	-2.92092066684743	1.32622813432498	-4.01410599867765
C	-2.26467588339790	0.79754341830096	-2.92871389225786
H	-4.11520080498012	2.94644694200182	-1.40368042404943
H	-4.47441619699379	2.94056312355605	-4.07742764407069
H	-2.77553485131929	1.04681785597711	-5.04642975996080
H	-1.50578553924184	0.03047042826232	-2.89138994573531
C	-0.57218383289684	-1.44979956157430	-0.37345237676430
C	0.76153713154468	-1.77536152848866	-0.40580864842932
H	-1.43594119135103	-2.07386224974216	-0.54413913323080
C	1.47243586163673	-0.59161292598800	-0.08621342417850
H	1.17657068212150	-2.74733284343338	-0.62512156082021
C	0.53066752955422	0.38592936339921	0.12120223993020
H	2.54253340129506	-0.47325160680121	-0.01104181603724

H	0.66529476144884	1.42213837269779	0.39257276466219
C	-1.65973060081959	3.60016814209981	0.55525370259810
C	-1.61355230883104	4.48279371197457	1.60655393823916
C	-2.09622424233991	3.78424398308466	2.74115762977235
H	-1.39142833038863	3.75000619554777	-0.47945205314921
H	-1.27862841398590	5.50795249458257	1.56483731224406
C	-2.40752355574211	2.51651064915022	2.31501185289621
H	-2.20397362752990	4.16564920437941	3.74508836488393
H	-2.80216444147806	1.68177644324322	2.87381042005348
O	-3.56132209162512	-0.20152681494794	0.61333923368139
C	-4.93772366865656	-0.09913430548003	0.43444027212667
C	-5.38280026579659	-0.84663222596842	-0.81919444080627
H	-5.25157156337731	0.95221010703732	0.31320385073870
C	-5.64497913701656	-0.63597743281870	1.67412002943900
H	-4.90631120938267	-0.43167812367875	-1.70838212919231
H	-6.46489740599642	-0.78142389940667	-0.95717235630211
H	-5.11289513334456	-1.90295047747335	-0.74831948195480
H	-6.73025277133043	-0.55619930710356	1.58066848674870
H	-5.33945123649746	-0.07981437646917	2.56152669849979
H	-5.39289985013777	-1.68675164795998	1.83301763077244

Pyrrole

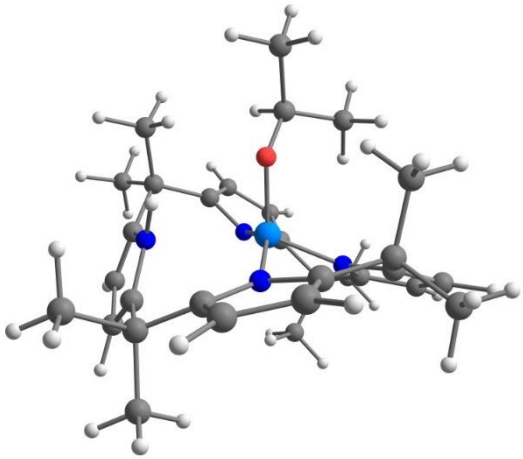


Total correction	0.08916040 E_h
Final entropy term	0.03109797 E_h
Final single point energy	-210.5397951 E_h
COSMO-RS correction (Gibbs free energy)	-18.5570 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-27.7344 kJ mol^{-1}

xyz 0 1

C	-3.16773312266824	1.49062639192866	0.00000004381216
C	-3.61143979057681	0.19492713414632	-0.00000004804130
C	-1.75164479768707	1.44976016180396	-0.00000003133579
C	-1.38338953079042	0.13063438566680	-0.00000000241988
N	-2.51995714076936	-0.61832453647875	0.00000003030930
H	-3.79022514050460	2.37009813267319	0.00000008123898
H	-4.61150174043874	-0.20470728236412	-0.00000008359443
H	-1.07946343698337	2.29186507103705	-0.00000004741657
H	-0.40803950112997	-0.32600876379494	0.00000000046400
H	-2.54888579845143	-1.62063069461818	0.00000005698351

syn-[(*i*PrO)-**1**-H]$^-$



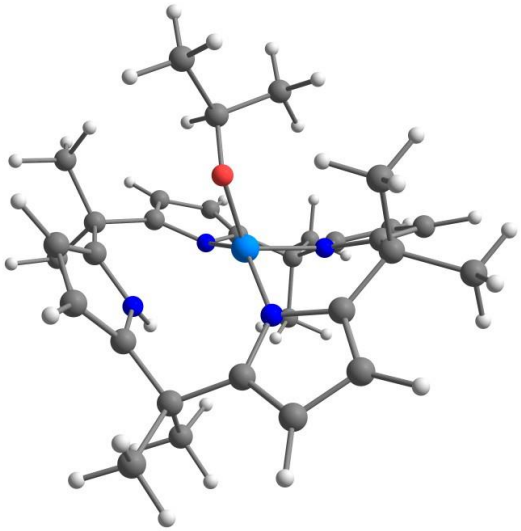
Total correction	0.71051872 E_h
Final entropy term	0.09246479 E_h
Final single point energy	-1745.178723 E_h
COSMO-RS correction (Gibbs free energy)	-201.9558 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-216.6230 kJ mol^{-1}

xyz -1 1

N	1.05779210416848	-1.74757653046231	1.72816285799472
C	2.04865767930727	-1.05316943176334	3.90504579739278
C	1.63082270052089	-2.22634606467565	4.81206272594924
H	2.35449805717003	-3.03962849724204	4.73487632646646
H	0.65093230570971	-2.61482267579950	4.53284427440728
H	1.57597633607748	-1.92152925835659	5.85756770198398
C	3.42274830417543	-0.54401251957717	4.36708057669209
H	4.17981933825782	-1.33155251924570	4.32931479193750
H	3.35890023735100	-0.18637482878964	5.39407592554515
H	3.75394024651253	0.28586381658634	3.74334560134030
N	0.67741890001590	0.94128999102988	3.01587625529395
C	0.03652466221804	2.00506907838465	3.63060326561219
C	1.04850611634049	0.07512258327252	4.02389814608109
C	-0.02510086763055	1.77890035307092	4.98641106682951
H	-0.46916600860461	2.42695826058658	5.72528485757376
C	0.61313109959885	0.55492299738241	5.23528613664431
H	0.79608527302284	0.11205616421218	6.20294658970041
C	-0.56086151013868	3.23518497185541	2.96333944510218
C	-2.08806154362670	3.05860617100772	2.83476752659742
H	-2.53840525355691	2.96113475002563	3.82526934495733
H	-2.33537866154108	2.16319412126382	2.27313734706330
H	-2.53218978360053	3.92175247938816	2.33357275223638
C	-0.32796361481322	4.44456401289103	3.88471482521463
H	-0.76284242688728	5.34397659968424	3.44700415527723
H	0.73500624809652	4.61966557327219	4.04499120019258
H	-0.80538570754133	4.30424368905349	4.85415421173082
N	0.57360432705567	2.59636863500556	0.80925077262520
C	1.07186040186611	3.20038162981016	-0.30524572540834
C	0.06748355362698	3.56012125436659	1.63262086772611
C	0.87072646004041	4.55650914479996	-0.21182589572354
H	1.16642466660240	5.30581936919865	-0.92996606412461
C	0.22658810686685	4.78691871640351	1.02766949984174
H	-0.06969151072381	5.74671298135806	1.42168430536103
C	1.84426690163645	2.39535976793569	-1.31035979146745
C	1.98409831427030	3.19598471695557	-2.60346793553431
H	2.48914362735153	4.14275373267011	-2.40857957766479
H	1.01102114420925	3.41659245268509	-3.04293085339959
H	2.58063181500310	2.65132404134048	-3.33655814919005
C	3.26164936574818	2.13184022220485	-0.75786507440149
H	3.85406347095189	1.56085386151927	-1.47646994030660
H	3.23091658344547	1.56100220594457	0.17002608367204
H	3.76980008416775	3.07608526462030	-0.55205176225344
N	0.96325360807395	0.12185943333373	-0.61512992898126
C	0.54878880862737	-1.02973917564832	-1.26483806101979
C	1.19206111945675	1.06495155026973	-1.59628933165785
C	0.47837643026414	-0.79304811611836	-2.61505016034113

H	0.22037077769298	-1.51138578726126	-3.37829614618851
C	0.88428316451475	0.54126358262757	-2.82748316406797
H	0.97480780397528	1.03928943535699	-3.77971665844666
C	0.45355897673225	-2.39683565665177	-0.60081338347006
C	-0.95680206617796	-2.79895650543760	-0.14359703876556
H	-1.63773511240924	-2.79590223669775	-0.99541567296425
H	-1.37377695882818	-2.12164328028714	0.59796745474627
H	-0.94630607164953	-3.80767431549471	0.27710648926072
C	0.92210260215815	-3.47177391497336	-1.58972005935639
H	0.22380273805804	-3.55912138680462	-2.42253216638667
H	0.97350715666604	-4.44341782641071	-1.09503001234934
H	1.90141304119494	-3.24066592246132	-2.00584695477109
C	2.17006308972829	-1.56212376251878	2.51184194408372
C	1.41054717635824	-2.35071059789898	0.54568192502583
H	0.11564926472740	-1.72648582296997	2.09229346422725
C	3.24568411677343	-2.01700614403430	1.80322255160664
H	4.27407008282725	-1.98400709954214	2.12450204438453
C	2.76468911057373	-2.51994910024028	0.56614868193379
H	3.36471602849824	-2.88254090286700	-0.25258841487237
Al	0.31807723019125	0.76549421533992	1.10430565318148
O	-1.35442805304795	0.25566358139955	1.10164392059597
C	-2.29067305068487	0.29399019001121	0.06232410119526
C	-3.64441853635487	-0.14210508889350	0.61408014175941
H	-2.01121489395721	-0.41529795912770	-0.73061003106452
C	-2.39988683244646	1.65757787705412	-0.61714448000031
H	-3.58141446553737	-1.13164729644527	1.07108764988525
H	-4.39733567767952	-0.18462638065495	-0.17600007285785
H	-3.99527601846981	0.55360627209554	1.37950110512533
H	-3.15617827754221	1.62093920340892	-1.40524318239442
H	-1.46042528461212	1.94915555540492	-1.08587820124933
H	-2.68133257041611	2.44378209926386	0.08436152862525

anti-[(^{i}PrO)-**1**-H]$^{-}$



Total correction	0.71038785 E_h
Final entropy term	0.09240566 E_h
Final single point energy	-1745.179903 E_h
COSMO-RS correction (Gibbs free energy)	-205.2013 kJ mol^{-1}
COSMO-RS correction (enthalpy)	-220.9374 kJ mol^{-1}

xyz -1 1

N	1.92629594482284	-1.70635304574131	1.46053441473173
C	2.84485366103300	-1.16614768107502	3.68676414960778
C	3.18509239453175	-1.97550482533229	4.93939616303127
H	3.68402872940095	-2.90573608916691	4.66322936847387
H	2.28964584311732	-2.22059986477471	5.50938999036489
H	3.85373738849922	-1.41842284033040	5.59553692820466
C	4.16598752681462	-0.79119957141644	2.98921611685766
H	4.71273795695218	-1.67451432534837	2.64811096105320
H	4.79901066982166	-0.24409472501292	3.68775688854301

H	4.01456879104375	-0.12418548233807	2.13749276602778
N	1.28078604722415	0.79526659076680	3.18712948836958
C	0.83505507199593	1.90414332209306	3.89369329623644
C	2.08749776083484	0.08777286902511	4.05200211664796
C	1.35650902337770	1.87797100102204	5.16391680515132
H	1.18521466674159	2.60276828215720	5.94308989149261
C	2.15334489662831	0.72319722637546	5.26524558979373
H	2.71290278876034	0.40248523445963	6.13006298551385
C	-0.14754705424942	2.94270943994120	3.38352529123207
C	-1.58990636908337	2.40730141937606	3.49859250651335
H	-1.82866209582399	2.21765191004336	4.54769806462494
H	-1.72667992627202	1.47850975286416	2.95382091547986
H	-2.29737964555209	3.14388975791266	3.10973217386182
C	-0.07591566807447	4.18554955177251	4.28006174780269
H	-0.77722282468431	4.94206913695113	3.92615980195629
H	0.92318130236025	4.62003566199514	4.28550439086186
H	-0.35975520260061	3.94668003167962	5.30550867711250
N	0.76421211939443	2.49598784800950	1.09338049316434
C	1.08747295929642	3.18477714562753	-0.03610328783814
C	0.20462810001404	3.36983458973418	1.98112499809634
C	0.70108399742811	4.49642069551044	0.10490636169065
H	0.83882639628729	5.29266171847493	-0.61054995121130
C	0.13273289967111	4.61409413634824	1.39690258152328
H	-0.25044305221311	5.51799544999374	1.84444000492018
C	1.94463397693159	2.52942145350617	-1.07880914908788
C	1.97497236928345	3.39698413780406	-2.33541151446534
H	2.34836886730520	4.39299212276371	-2.09513132985552
H	0.98059338607069	3.50401363705487	-2.76920485324096
H	2.63840904636469	2.97191111935568	-3.08981944208683
C	3.38774819449742	2.43431540887835	-0.53738014027520
H	4.04402117006053	1.95711930659729	-1.26913661811907
H	3.43165244279013	1.85401606805562	0.38499040786622
H	3.77566749702997	3.42946659521290	-0.31152857766966
N	1.29355808703116	0.14572319229574	-0.47803986871722
C	0.98641579935224	-1.00823542847612	-1.18686342745703
C	1.46486324046471	1.14232969109207	-1.42065580668680
C	0.95080944921051	-0.72637299274153	-2.52934141846532
H	0.75220614626153	-1.43258115964009	-3.32244380419804
C	1.25269381585051	0.63999385149134	-2.67981498369591
H	1.31978396068194	1.18335636482134	-3.60858672774286
C	0.85512097458231	-2.42371559364690	-0.64527397185311
C	-0.46727776546474	-3.06591001488041	-1.07353145559993
H	-0.57261664184833	-3.03835029150627	-2.15765425116030
H	-1.31966892484171	-2.54936058427841	-0.63868726677715
H	-0.50748146577298	-4.11277823560501	-0.76348334018289
C	2.00394529528754	-3.27350222171576	-1.24006025322071
H	1.93731281753089	-3.31004705906817	-2.32794445834402
H	1.96477482467942	-4.29455623560555	-0.85429838324826
H	2.97965289338668	-2.85405857001357	-0.99086194275558
C	1.98173971168128	-1.99819997536500	2.79746901498893
C	0.97866329456730	-2.47805544781571	0.83746021796622
H	2.67419515906011	-1.26272136873725	0.95192940528053
C	1.01648731481179	-2.93188218993742	3.04240482341656
H	0.73940871422015	-3.31319001885950	4.01197854088667
C	0.38499566385054	-3.23727403686184	1.80278252580899
H	-0.43847073363751	-3.91751268243964	1.65572191945000
Al	0.66956746556913	0.62770145214975	1.33342533295207
O	-0.94224392257996	-0.00211130393032	1.39096167320003
C	-1.92429797636121	-0.00877630142359	0.40334086429672
C	-3.08881895002140	-0.86886401867373	0.88292487068021
H	-1.53813145584893	-0.45607733813675	-0.52587486968868
C	-2.40513907244573	1.39285046027899	0.03253637640073
H	-2.74440028194065	-1.87082023357195	1.14482702038921
H	-3.86024693424207	-0.95999058904770	0.11480678784893
H	-3.54658470939196	-0.43349360493645	1.77412866096404
H	-3.16965029297156	1.33794642263924	-0.74676136112365
H	-1.58976370151898	2.00786896488340	-0.34987616593393
H	-2.83614384702414	1.90971292643685	0.89138424936368

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